

A scanning electron micrograph (SEM) showing the intricate, porous structure of an electrospun membrane. The image displays a dense network of randomly oriented nanofibers, creating a highly porous, non-woven fabric. The fibers vary in thickness and are interconnected, forming a complex mesh-like structure. The background is dark, highlighting the fine details of the fibrous network.

Advanced Functionalized Electrospun Membrane for Water Treatment: Comparing Low Frequency Ultrasound Effects on ENMs and PES Membranes in CNC Filtration

Department of Process and Life Science Engineering | LUND UNIVERSITY

Golshan Sabbaghian | THESIS 2025



Advanced Functionalized Electrospun Membrane for Water Treatment:

Comparing Low Frequency Ultrasound Effects on ENMs and
PES Membranes in CNC Filtration

by

Golshan Sabbaghian

Division of Chemical Engineering
Department of Process and Life Science Engineering
Lund University

August 2025

Supervisor: **Professor Frank Lipnizki**
Co-supervisor: **Assistant Professor Nicolas Hengl**
Examiner: **Professor Ola Wallberg**

Picture on front page: SEM of Electrospun Membrane at IMFT. Photo by Golshan Sabbaghian

Postal address

Box 124
SE-221 00 Lund, Sweden

Web address

<http://www.ple.lth.se>

Visiting address

Kemicentrum
Naturvetarvägen 22
223 62 Lund, Sweden

Telephone

+46 46-222 82 85
+46 46-222 00 00

Acknowledgment

This master thesis project has been conducted as part of the Erasmus Mundus Joint Master in *Membrane Engineering for Sustainable Development (MESD)*, funded by the European Union.

The AFEM (Advanced Functionalized Electrospun Membrane for water treatment) project is conducted within the framework of the Unite! (University Network for Innovation, Technology and Engineering) alliance, a collaboration of nine European universities committed to innovation, sustainability and excellence in science and engineering education. The AFEM project integrates expertise from several institutions: *Politecnico di Torino* (membrane fabrication), *Technische Universität Darmstadt* (catalytic modification), and *Université Grenoble Alpes / IMFT Toulouse* (ultrasound-assisted fouling control). The current study focuses on the third aspect, fouling control using ultrasound and was carried out at the *Institut de Mécanique des Fluides de Toulouse (IMFT)*.

The author thanks the European Commission - Education, Audiovisual and Culture Executive Agency (EACEA) for the Erasmus Mundus scholarship under the program: Master in Membrane Engineering for Sustainable Development (MESD), Project number: 101081874, Call: ERASMUS-EDU-2022-PEX-EMJM-MOB

EN Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Education and Culture Executive Agency (EACEA). Neither the European Union nor EACEA can be held responsible for them.

FR Financé par l'Union européenne. Les points de vue et avis exprimés n'engagent toutefois que leur(s) auteur(s) et ne reflètent pas nécessairement ceux de l'Union européenne ou de l'Agence exécutive européenne pour l'éducation et la culture (EACEA). Ni l'Union européenne ni l'EACEA ne sauraient en être tenues pour responsables

SV Finansieras av Europeiska unionen. De synpunkter och åsikter som uttrycks är endast upphovsmannens [upphovsmännens] och utgör inte Europeiska unionens eller Europeiska genomförandeorganet för utbildning och kulturs (EACEA) officiella ståndpunkt. Varken Europeiska unionen eller EACEA tar något ansvar för dessa.

Preface

*“What you seek is not beyond you;
turn inward, for within you lies all that you desire.” – Rumi*

These words have been a guide throughout my thesis journey. More than an academic project, this work has been a path of self-discovery, of learning patience, resilience, and trust in myself. There were moments when progress felt slow and challenges seemed overwhelming, but step by step I discovered that the strength to continue was always within me. This thesis is therefore not only the outcome of research, but also a chapter of personal growth and transformation.

I am deeply grateful to Nicolas Hengl, whose insightful guidance, constructive feedback, and constant encouragement shaped both this work and my development as a researcher. His trust and patience gave me the confidence to persevere, even in difficult moments. I also sincerely thank Frank Lipnizki for his thoughtful advice and steady support, which have been invaluable throughout this project.

To my colleagues and friends, I owe heartfelt thanks. I learned that the true beauty of friendship shines most in hard times, in shared challenges, long discussions, and the laughter that lightened even the heaviest days. Your presence turned effort into memory and work into something joyful.

To my dearest parents, Sharareh and Reza: though miles have kept us apart for two years, all that I am and all that I hope to become is rooted in you. No distance can ever lessen your presence in my heart; I carry your love and strength with me in every step I take. Even across the distance, I am always by your side. This thesis is only a small accomplishment, just the beginning of my journey, and it belongs to you as much as it belongs to me.

Popular Scientific Summary

Water is something most of us take for granted, turn on the tap, and there it is. But for many people around the world, clean water is becoming harder to find. Pollution, climate change, and industrial waste are making it more difficult to treat and reuse water safely. As these problems grow, scientists are working on more sustainable ways to clean water.

One of the most promising tools for water purification is a membrane, a thin filter that lets clean water through while blocking dirt, bacteria, and other unwanted particles. However, over time, even the best membranes can get clogged up, this problem is known as fouling, and it's one of the biggest challenges in water treatment today.

This research looked at a way to reduce this fouling: by using sound waves. Not the kind we hear with our ears, but high-frequency vibrations known as ultrasound. These sound waves can shake and loose the particles stuck on the membrane's surface, helping to keep it clean and working better for longer times.

Two types of membranes were tested in this project for the filtration of the cellulose nanocrystal (CNC) suspensions under ultrasound. One was a commercial polyethersulfone (PES) membrane, commonly used in water treatment applications. The other was made from electrospun nanofibers, fabricated at Politecnico di Torino University in Italy.

The Filtration tests showed that applying ultrasound during operation significantly reduced fouling and improved water flow. In some cases, membranes maintained nearly 100% of their initial water flux, meaning they stayed efficient over time. The electrospun nanofibers membranes (ENMs) responded particularly well to ultrasound, remaining intact without visible damage. However, their flux behavior varied, likely due to differences in their structure and non-uniformity in the way they were manufactured.

To better understand how CNC particles accumulated on the membrane during filtration, a technique called Small-Angle X-ray Scattering (SAXS) was used. This advanced method can be used to see how particles were distributed layer by layer on the membrane surface and how fouling develops over time and provided deeper insight into how ultrasound helps reduce it.

Another unique aspect of this research was that, unlike traditional membranes, electrospun membranes had never been tested with ultrasound during filtration. By comparing these ENMs to the PES membranes under the same conditions, with and without ultrasound, clear differences in how they responded can be analyzed.

Summary

This thesis investigates how low-frequency ultrasound can enhance membrane filtration performance and reduce fouling, one of the most critical limitations of membranes in water treatment technologies. Two types of membranes were studied. Flat-sheet polyethersulfone (PES) membranes, widely used for their mechanical and chemical stability, and electrospun nanofiber membranes (ENMs) made from styrene-butadiene rubber (SBR), which offer high porosity and permeability. Experiments were conducted in both dead-end and crossflow filtration setups using cellulose nanocrystals (CNCs) as a model foulant. While PES membranes provided stable performance under various conditions, ENMs showed higher initial flux but were more sensitive to fouling and structural degradation, especially in unsupported or thin configurations. Applying ultrasound improved filtration performance in both systems by increasing water flux and partially mitigating fouling, particularly during active ultrasound phases. Notably, this study is among the first to systematically explore the direct application of ultrasound to electrospun membranes during active filtration, an area that had previously remained largely unexamined, despite its promising potential for enhancing membrane performance. To understand the structural dynamics behind fouling, Small-Angle X-ray Scattering (SAXS) was used to analyze how CNCs build up on the membrane over time. This analysis revealed concentration gradients and particle accumulation near the membrane surface, offering valuable insight into the stages of fouling.

Keywords: Membrane Engineering, Electrospun Membranes, Ultrasound-assisted Filtration, Membrane Fouling, Polyethersulfone Membranes, SAXS, Nanofiber structure, Water Treatment

List of Abbreviations

CNC	Cellulose Nanocrystals
ENM	Electrospun Nanofiber Membrane
PES	Polyethersulfone
SAXS	Small Angle X-ray Scattering
SBR	Styrene Butadiene Rubber
UF	Ultrafiltration
US	Ultrasound

Table of Contents

1	Introduction	1
1.1	Aim	2
1.2	Research Gap Statement	2
2	Literature Review	3
2.1	Membrane Technology in Water treatment	3
2.2	Polyethersulfone Ultrafiltration Membranes	4
2.3	SBR Electrospun Nanofiber Ultrafiltration Membranes	4
2.4	Membrane Filtration Modes: Dead-End vs. Crossflow	4
2.5	Membrane Fouling	5
2.6	Ultrasound	9
2.7	Ultrasound Application in Membrane Fouling and Cleaning	12
2.8	Small angle X-ray scattering (SAXS)	16
3	Materials and Methods	17
3.1	Filtered Suspensions and Tested Membranes	17
3.2	Ultrasound-assisted Filtration Set up	17
3.3	Experimental Procedure for PES Membranes	19
3.4	Experimental Procedures for ENMs	22
3.5	Observed Parameters during the Filtration	25
3.6	Dead-End Filtration under SAXS Measurements	28
4	Results & Discussions	33
4.1	Permeability of PES Membranes	33
4.2	Effect of US on CNC Filtration with PES Membranes	35
4.3	Characterization of PES Membrane Filtration using SAXS	39
4.4	Permeability of ENMs Membranes	42
4.5	Effect of US on CNC Filtration with ENMs	43
4.6	Structural Analysis of ENMs	47
4.7	Comparison Between ENMs and PES Membranes	53
5	Conclusion & Future Studies	55
	References	57
	Appendices	67

1 Introduction

Freshwater resources are under growing pressure due to several global challenges such as increasing population, climate change, and the rise of industrial activities. These issues have reduced both the amount and quality of available freshwater. As a result, there is a strong need for better water treatment solutions. One of the most promising approaches is membrane filtration, which is now widely used to treat both drinking water and wastewater because of its ability to remove various types of pollutants efficiently with relatively low energy use (Wang *et al.*, 2024).

One important challenge in using membrane processes effectively is the drop in performance caused by membrane fouling. This occurs when very small particles, such as micro- and nanoparticles, accumulate on the membrane surface or clog its pores, leading to a reduction in membrane efficiency (Zhang *et al.*, 2019; Aghapour Aktij *et al.*, 2020). Both Electrospun Nanofibrous Membranes (ENMs) and Polyethersulfone (PES) membranes are widely used in water treatment due to their strong filtration performance, however, membrane fouling remains a major issue with these membranes (Chen *et al.*, 2020; Rattana-arporn and Poompradub, 2024). Traditional methods for reducing membrane fouling are often difficult to apply and can lead to long-term damage to the membrane. A more efficient and less harmful alternative is ultrasound technology, which uses sound waves to remove particles that accumulate on the membrane surface. This technique enhances the detachment of foulants and improves mass transfer near the membrane, leading to a more effective reduction of fouling and better overall membrane performance (Zhang *et al.*, 2019).

Based on the extent of foulant attachment to the membrane surface, fouling can be reversible or irreversible, requiring physical or chemical cleaning (Aghapour Aktij *et al.*, 2020). To reduce membrane fouling, researchers have combined membranes with methods like adsorption, electrochemical treatments, and advanced oxidation. Recent studies suggest that ultrasound can improve permeability and help to maintain consistent filtration performance (Borea *et al.*, 2018). Its efficiency is primarily attributed to the dynamic physical effects generated through ultrasonic cavitation. This process produces phenomena such as acoustic streaming, microstreaming, microstreamers, microjets, shock waves, and heating which aid in enhancing permeate flux (Aghapour Aktij *et al.*, 2020).

Ultrasound has shown significant potential in enhancing the performance of ultrafiltration, particularly in both crossflow and dead-end filtration systems. (Zhang *et al.*, 2019). Polyethersulfone is a commonly used material for ultrafiltration membranes due to its favorable mechanical strength, chemical stability, and affordability (Desiriani *et al.*, 2024). The performance of PES membranes often declines over time due to fouling, which increases operational energy demands. This typically results from the formation of a fouling layer and pore blockage, caused by the gradual accumulation of contaminants on the membrane surface. Their hydrophobic nature makes PES membranes more prone to attracting organic matter, microorganisms, and colloidal particles, accelerating the fouling process (Mulyati *et al.*, 2025).

The electrospinning process enables the fabrication of lightweight, nanofibrous polymer membranes by using high-voltage electrostatic forces applied to a polymer solution (Chen *et al.*, 2020). This method is a practical and low-cost fabrication technique for creating fibrous membranes with high porosity and a large surface area (Maurya *et al.*, 2022).

Despite growing interest in ultrasound-assisted membrane processes, the direct impact of in-situ ultrasound on the filtration performance of electrospun membranes remains largely unexamined. Gaining fundamental insight about this research gap is critical for future electrospun membrane fabrication and optimization under ultrasound.

1.1 Aim

The primary aim of this study is to investigate the effect of low-frequency ultrasound (20 kHz) on the structural properties, fouling behavior, permeability of the ENMs made from styrene-butadiene rubber (SBR), developed at Politecnico di Torino, in comparison with PES membranes. The membranes will be tested during cellulose nanocrystal (CNC) filtration under both dead-end and crossflow configurations, with performance evaluated through measurements of permeation flux and fouling behavior. Structural stability before and after ultrasound exposure will be assessed using scanning electron microscopy (SEM) to examine surface morphology and small-angle X-ray scattering (SAXS) to analyze nanoscale structural organization.

1.2 Research Gap Statement

Despite growing interest in ultrasound-assisted membrane filtration, no systematic studies have been reported on the performance and structural integrity of electrospun nanofiber membranes under continuous ultrasound exposure during active operation. Although ultrasound has been applied to other membranes in various cleaning and enhancement contexts, its direct integration into real-time filtration with electrospun membranes remains largely unexamined. This work takes an initial step toward filling that gap by investigating the behavior of electrospun membranes under dynamic conditions and comparing their performance to polyethersulfone membranes for the application of sustainable water treatment.

2 Literature Review

2.1 Membrane Technology in Water treatment

Population growth, climate change, and industrialization are among the main factors increasing water demand and putting greater pressure on already limited water resources. These challenges have made the global shortage of clean water more severe. At the same time, rapid economic development and human activities have led to increased pollution, as industries and communities frequently release wastewater, solid waste and accidental discharges into the environment. This growing pressure highlights the need to use water resources in a sustainable way, which is essential for the long-term development of both society and economy. To help manage this issue, membrane technologies and related methods are being used to remove pollutants from water and wastewater. These systems make it possible to safely use alternative water sources, supplementing the limited supply naturally available through the Earth's water cycle (Awad *et al.*, 2021a; Wang *et al.*, 2024).

Many natural water sources are not clean enough for drinking and must go undergo proper treatment to meet safe standards for household use (Fetyan and Salem Attia, 2020). According to HMTShirazi *et al.* (HMTShirazi *et al.*, 2022), current water treatment methods can be categorized into five main groups, as illustrated in Figure 2.1. Water treatment systems often face several difficulties, such as high operational costs, limited efficiency in removing certain pollutants, system maintenance issues, and the production of harmful by-products during the treatment process (Fetyan and Salem Attia, 2020).

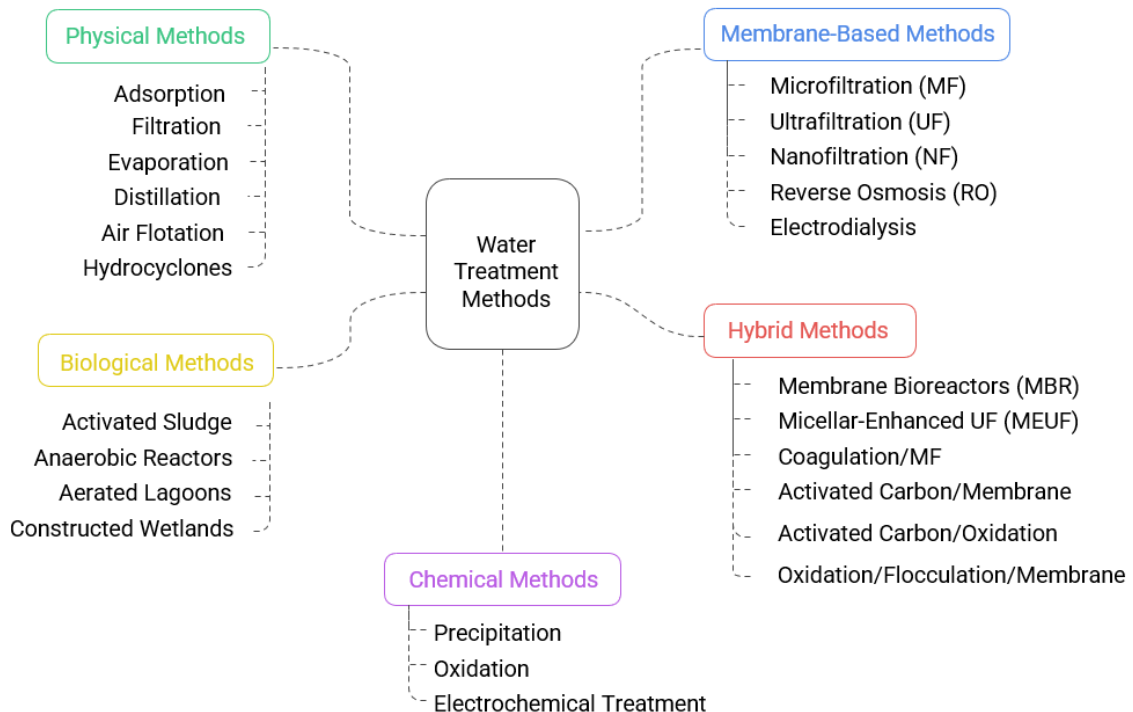


Figure 2.1 Water treatment methods, Adapted from HMTShirazi *et al.* (2022).

2.2 Polyethersulfone Ultrafiltration Membranes

Ultrafiltration (UF) is a membrane separation process that has been widely used in industrial applications such as concentration, fractionation, and the removal of large molecules from wastewater streams. It plays an important role in water treatment, especially in separating macromolecular substances from complex effluents (Naji *et al.*, 2021). UF membranes typically have pore sizes ranging from 2 to 100 nanometres and can effectively separate proteins, polypeptides, and suspended solids. The process operates at relatively low pressures, usually between 1 and 2 bar, and is known for being energy-efficient, easy to operate, and cost-effective (Li *et al.*, 2025).

Polyethersulfone (PES) polymers are used to make UF membranes for treating wastewater (Awad *et al.*, 2021b). The separation ability of UF membranes depends on the membrane's pore size compared to the size of the target chemicals. UF membranes made from polymers like PES, cellulose and polyacrylonitrile are often created through phase inversion, which produces a nearly uniform distribution of pore sizes (Zuo *et al.*, 2021). These membranes are often prepared using the phase inversion method, a widely adopted technique that creates an asymmetric structure (Idris, Mat Zain and Noordin, 2007).

Despite their advantages, UF membranes also have limitations. Their separation mechanism is not effective for removing dissolved salts and smaller organic molecules, which can pass through the pores (Zulu *et al.*, 2025). In addition, membrane fouling is a major issue in UF systems, as it lowers water flux and increases both processing and maintenance expenses (Naji *et al.*, 2021).

2.3 SBR Electrospun Nanofiber Ultrafiltration Membranes

Electrospun nanofibers are considered strong candidates for advanced applications because of their unique and beneficial structure offering high porosity, and large surface-to-volume ratio. These characteristics make them ideal for a wide range of uses, including water filtration, drug delivery systems, biosensors, tissue engineering, and energy storage devices (Fan *et al.*, 2018; Maurya *et al.*, 2022). Electrospun nanofiber layers enhance ultrafiltration membranes by increasing water permeance, reducing fouling, and preserving separation performance (Dobosz *et al.*, 2017). Styrene-butadiene rubber (SBR) is a synthetic rubber widely used in industry because of its excellent flexibility, abrasion resistance, and long-term durability. It is commonly produced through cold emulsion copolymerization at around 5 °C using a series of six to fifteen continuously stirred reactors (Zubov, Pokorný and Kosek, 2012).

2.4 Membrane Filtration Modes: Dead-End vs. Crossflow

Filtration processes can be performed in various ways, with dead-end and crossflow filtration being the two most commonly used methods today (Yao Jin, 2014).

In dead-end filtration, the feed flows perpendicularly toward the membrane and passes through it entirely, with no reject stream. This leads to continuous solute buildup on the membrane surface, forming a uniform cake layer that causes a steady decline in flux. While feed-side agitation can reduce this effect, the rapid drop in productivity makes this mode less practical for large-scale applications (Yao Jin, 2014; Ehsani, Doan and Lohi, 2021a).

In contrast, crossflow filtration moves the feed tangentially across the membrane, creating turbulence that minimizes particle accumulation. This results in a slower decline in flux and better

long-term performance, making crossflow the preferred method in industrial membrane systems (Yao Jin, 2014; Ehsani, Doan and Lohi, 2021a).

2.5 Membrane Fouling

A clear understanding of membrane fouling and the mechanisms behind it is essential for developing new strategies to control fouling and improve membrane cleaning methods. For this reason, this section introduces the basic principles related to membrane fouling.

2.5.1 Principle of Fouling

Membrane fouling is a well-known issue in MF and UF systems applied in industries, including bioprocessing and dairy, as well as in water and wastewater treatment applications (Xu *et al.*, 2020; Tanudjaja *et al.*, 2022). Membrane technologies are effective for removing various contaminants such as microorganisms, organic matter, inorganic salts, and suspended solids. They aim to provide high rejection rates and consistent permeate flow. However, solute accumulation on the membrane surface (external fouling) and within its pores (internal fouling) leads to reduced performance due to complex physical and chemical interactions. Membrane fouling is a complex process involving multiple physical and chemical mechanisms that work together and affect performance (Hilal *et al.*, 2005). The overall effect of fouling is a decrease the active membrane area or an increase in the resistance across the membrane leading to a decreased flux for a given TMP. Common fouling mechanisms include adsorption, pore blocking, particle accumulation, and gel layer formation (Peinemann and Pereira Nunes, 2010).

2.5.2 Types of Membrane Fouling

These mechanisms are generally classified into four main types, based on how foulants interact with the membrane.

Adsorption

Adsorption occurs when foulants attach to the membrane surface or within the pore walls through specific interactions. This attachment raises hydraulic resistance and reduces membrane efficiency (Qasim *et al.*, 2018).

Pore Blockage

Pore blockage happens when particles clog the membrane pores, restricting water flow and lowering flux across the membrane (Qasim *et al.*, 2018).

Cake Formation

Deposition involves the gradual buildup of foulants in layers on the membrane surface. This leads to additional resistance, known as cake resistance, which further reduces filtration performance (Qasim *et al.*, 2018).

Gel layer Formation

Gel fouling takes place when large molecules, such as proteins or colloidal substances, accumulate on the membrane surface and form a dense, cross-linked, three-dimensional network. Since the gel blocks or narrows the membrane pores, it disrupts the flow path and increases resistance to mass transport, leading to a noticeable drop in filtration efficiency (Qasim *et al.*, 2018).

2.5.3 Effective Parameters in Fouling

This section discusses the key factors that influence membrane fouling, including fouling type, membrane properties, feed solution characteristics, operating conditions.

Types of Fouling

The type of foulants present in the feed solution is a key factor influencing membrane fouling (Ehsani, Doan and Lohi, 2021a). Depending on the feedwater composition, foulants are generally grouped into four categories: organic substances that tend to adsorb onto the membrane surface, inorganic materials that may precipitate due to changes in pH or oxidation, particulate or colloidal matter that can block pores or form a surface layer, and microorganisms that cause biofouling through attachment and growth (Qasim *et al.*, 2018). Figure 2.2 illustrates the four main types of membrane foulants, along with representative examples of each category.

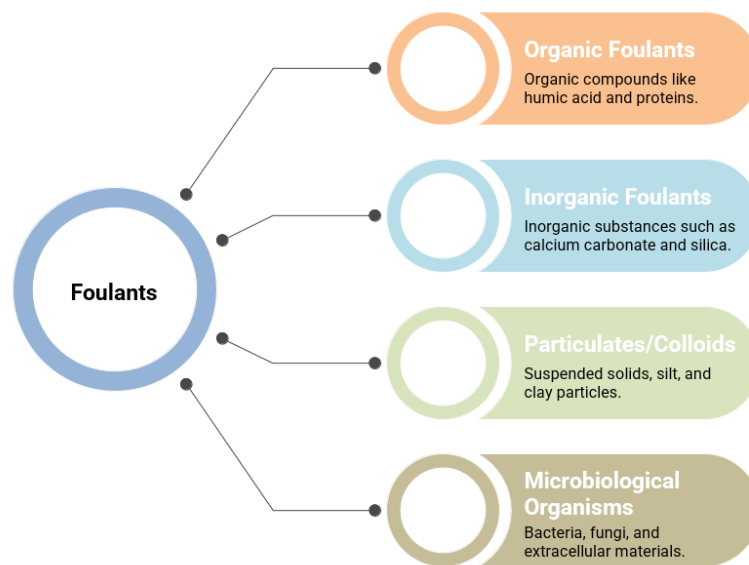


Figure 2.2 Classification of membrane foulants, Adapted from Qasim *et al.*(2018).

Membrane Properties

In industrial applications, membranes are usually made from either polymers or inorganic materials, depending on the needs of the process. To be effective, membranes need to handle changes in temperature, pressure, and pH, and resist damage from repeated cleaning and exposure to various chemicals. They can be either hydrophilic or hydrophobic. Hydrophilic membranes are preferred in processes that require high water flux because they attract less fouling (Ehsani, Doan and Lohi, 2021a). On the other hand, hydrophobic membranes repel water and therefore have a limited capacity to adsorb it (Koo *et al.*, 2012).

Membrane Surface Pore Size

Membrane pore size plays a key role in how fouling develops. It has been found that fouling reversibility is influenced by the membrane's intrinsic pore size, with irreversible fouling

occurring more frequently in membranes that have larger pores (Qu *et al.*, 2014). Membranes with larger pore sizes are more susceptible to internal fouling, as larger particles can penetrate deeper into the pores, making the fouling more difficult to remove over time (Nghiem and Hawkes, 2007; Qu *et al.*, 2014). Membranes with smaller pores are more prone to gradual surface blockage, as materials build up either on the surface or inside the pores, eventually reducing the available pore space (Ehsani, Doan and Lohi, 2021b).

Flow Velocity

Flow velocity strongly affects membrane performance and fouling behavior. As studied by Chen *et al* (2018) increasing cross-flow velocity effectively reduces the rate of fouling formation. This is because higher flow velocities generate greater turbulence at the membrane surface, which helps prevent foulants from settling and accumulating, thereby improving overall membrane performance (Bolton, Boesch and Lazzara, 2006).

Process Pressure

Operating pressure also plays a crucial role in the fouling process. Jain, Sengupta, and De (2018) observed that at lower transmembrane pressures, fouling primarily occurs through pore blockage, which can be mitigated by increasing the cross-flow rate. In contrast, at higher transmembrane pressures, fouling is mainly due to cake formation, and changes in feed flow rate have limited impact because of the compressibility of the fouling layer.

2.5.4 Fouling Control

Despite advancements in fouling-resistant materials, membrane fouling remains unavoidable. Thus, effective control strategies and regular cleaning are essential to maintain performance and extend membrane life (Kallioinen and Mänttari, 2011). Fouling is generally categorized as reversible or irreversible. Reversible fouling can usually be removed through physical cleaning methods such as backwashing or surface flushing. In contrast, irreversible fouling, which remains after physical cleaning, requires chemical treatment to be eliminated (Ehsani, Doan and Lohi, 2021a). Fouling can be minimized by adjusting interactions between particles and the membrane, often through feed pretreatment. Chemical cleaning with acids, alkalis, or biocides is widely used to remove inorganic, organic, or biological fouling, typically restoring membrane performance. Physical cleaning methods, such as backwashing or air scouring, help dislodge surface particles but may not suit all feed types. Advanced techniques like electric pulses or ultrasound can also reduce buildup. The frequency and intensity of both chemical and physical cleaning significantly affect membrane lifespan and overall operating costs (Camara, Doan and Lohi, 2020).

Membrane fouling can be addressed through two main strategies, cleaning techniques and fouling control methods. Cleaning approaches include physical, chemical, and biological processes aimed at removing accumulated materials from the membrane surface. In contrast, control methods such as feed pretreatment and membrane surface modification are used to reduce the rate of fouling and extend membrane life (Ehsani, Doan and Lohi, 2021b). These strategies are summarized in Figure 2.3, which outlines the key methods used to manage membrane fouling.

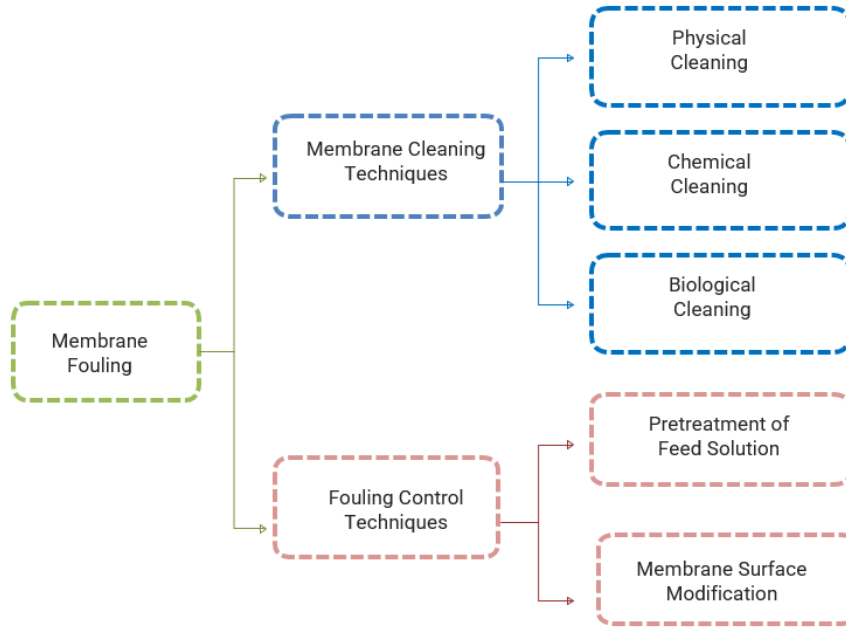


Figure 2.3 Membrane fouling control and cleaning methods, Adapted from Ehsani, Doan and Lohi (2021b).

2.5.5 Membrane Resistance and the Resistance-in-Series Model

Membrane resistance to permeate flow changes depending on the type of fouling. Standard pore-blocking increases resistance (R_p) while cake formation introduces additional resistance (R_c), both contributing to the overall decline in filtration performance (Juang, Chen and Chen, 2008).

To better describe these effects, the resistance-in-series model is commonly applied, particularly in UF and MF systems (Juang, Chen and Chen, 2008). The total resistance to filtration, R_{tot} , is expressed in Equation (2.1) and (2.2) and it is derived from Darcy's law.

$$R_{tot} = \frac{TMP}{\mu \cdot J} \quad (\text{Eq. 2.1})$$

where J is the permeate flux ($\text{m}^3/\text{m}^2/\text{s}$), TMP is the transmembrane pressure (Pa), and μ is the permeate viscosity ($\text{Pa}\cdot\text{s}$). Moreover, fouling development can be studied by keeping either TMP or J constant, while allowing the other to vary. Moreover, fouling can be investigated by examining the reversibility of the cake layer formed on the membrane surface (Di Bella and Di Trapani, 2019).

When particles larger than the membrane pores accumulate on the surface, it leads to cake deposition, which primarily causes reversible fouling. A small fraction of this deposition can result in irreversible fouling, but this is typically minimal and often disregarded, depending on the operating conditions and the type of membrane model used (Di Bella and Di Trapani, 2019).

$$R_{tot} = R_m + R_f + R_c \quad (\text{Eq. 2.2})$$

$R_f (\text{m}^{-1})$ represents the irreversible fouling resistance that permanently affect the membrane, while $R_c (\text{m}^{-1})$ is the resistance caused by cake deposition on the membrane surface and $R_m (\text{m}^{-1})$ is the resistance of the membrane (Di Bella and Di Trapani, 2019). Furthermore, some studies also show that additional resistance occur due to surface or pore adsorption R_{ads} independently of flux and is measured by first contacting the membrane with the feed without applying flux and then measuring the pure solvent flux at a known TMP (Field and Pearce, 2011).

Fouling behavior can also be evaluated under different operation modes. In constant TMP mode, the initial flux is high because the resistance is low, but it declines over time as fouling increases. This change alters local hydrodynamics. Conversely, in constant flux mode, the TMP rises as resistance builds up, allowing for a clearer observation of fouling progression while keeping flow conditions more stable (He *et al.*, 2017).

2.6 Ultrasound

Ultrasound has emerged as a promising alternative approach for membrane cleaning and fouling mitigation. Its application generates localized turbulence at the membrane surface through different phenomena, which facilitates the displacement of foulants adhered to the membrane. By disrupting the fouling layer, ultrasound reduces the total resistance to permeate flow, thereby enhancing membrane performance (Camara, Doan and Lohi, 2020). Ultrasound has emerged as a promising technique for mitigating membrane fouling in both UF and MF systems and it can enhance performance in both crossflow and dead-end filtration configurations (Liu *et al.*, 2013).

2.6.1 Principle of Ultrasound

Ultrasound, or ultrasonic sound waves, refers to acoustic longitudinal vibrations with frequencies above 20 kHz, beyond the range of human hearing. (Qasim *et al.*, 2018; Yao, Pan and Liu, 2020)

2.6.2 Generation and Propagation

Ultrasonic waves travel through longitudinal motion involving alternating compression and rarefaction, which generates variations in pressure across space and time as they move through a medium (Leighton, 2007). Ultrasonic transducers are specialized devices that convert electrical or mechanical energy into high-frequency sound waves known as ultrasound. Two types of transducers commonly utilized in industrial settings are magnetostrictive and piezoelectric transducers (Yao Jin, 2014; Yao, Pan and Liu, 2020).

Magnetostrictive transducers work by using a magnetic coil and a vibrating material, such as nickel or Terfenol-D, to produce mechanical vibrations from electrical energy. On the other hand, piezoelectric transducers use piezoelectric crystals that vibrate when an electric signal is applied. These crystals are typically mounted between metal plates and are attached to a vibrating piece like a probe or sonotrode, allowing the conversion of electrical signals into ultrasonic waves (Fetyan and Salem Attia, 2020; Yao, Pan and Liu, 2020). Piezoelectric transducers offer several practical advantages over their magnetostrictive counterparts, including a simpler structure, higher energy efficiency, lower production cost, and the absence of electromagnetic

radiation. As a result, they have become the preferred choice in both industrial and research settings (Yao, Pan and Liu, 2020).

2.6.3 Phenomena of Ultrasound

Ultrasound is capable of generating a range of physical phenomena within heterogeneous solid–liquid systems, which can facilitate the detachment of particles adhered to fouled membrane surfaces. These phenomena are acoustic streaming, microstreaming, as well as the development of microjets, microstreamers, and shock waves (Qasim *et al.*, 2018).

Acoustic Cavitation

When ultrasonic waves propagate through a liquid medium, the molecules within the fluid are subjected to alternating cycles of compression and rarefaction aligned with the direction of wave travel. These oscillatory pressure variations result in the generation of an additional acoustic pressure (P_a) that acts alongside the hydrostatic pressure (P_0) of the fluid (Qasim *et al.*, 2018). The frequency of the applied ultrasound significantly affects how microbubbles within a liquid behave. Depending on the frequency, these bubbles can be stimulated to oscillate in response to the alternating pressure waves. This oscillation produces shear forces that improve fluid movement and increase mass transfer efficiency, which can be beneficial in various chemical processes (Yusof *et al.*, 2016a). During the compression phase, positive acoustic pressure forces molecules closer together, while the rarefaction phase generates negative pressure that draws the molecules apart. If the tensile stress created during rarefaction exceeds the liquid's cohesive strength, the intermolecular forces are unable to maintain structural integrity, resulting in the formation of vapor-filled cavities known as cavitation bubbles (Qasim *et al.*, 2018). Typically, the bubbles grow to a maximum size of 2–150 μm (Fang, Qi and Smith, 2015).

After cavitation bubbles are formed, they can either shrink and disappear or continue to grow. Their growth usually happens through two main processes: coalescence, where smaller bubbles join together, and rectified diffusion, where gas enters the bubble more during the low-pressure (rarefaction) phase than it escapes during the high-pressure (compression) phase. This happens because the surface area available for gas exchange is different in each phase, an effect known as the area effect (Yusof *et al.*, 2016a). Alongside the area effect, the shell effect is a critical factor in rectified diffusion (Bhangu and Ashokkumar, 2016). It describes how the liquid layer around a cavitation bubble changes during ultrasound cycles. In compression, the shell thickens, limiting gas release and in rarefaction, it becomes thinner, allowing more gas to enter. This imbalance promotes gradual bubble growth over time (Qasim *et al.*, 2018). As a result, the overall effect is a gradual increase in bubble size (Leighton, 1994). When the bubble reaches a certain critical size, called the resonance size, it may suddenly collapse with great force, in what is known as acoustic cavitation (Yusof *et al.*, 2016a).

When cavitation bubbles collapse in aqueous systems, they generate intense physical and chemical effects that initiate fluid movement (Hengl *et al.*, 2014a). At low ultrasonic frequencies, even small bubbles that have not reached their resonance size can still undergo cavitation and produce useful physical and chemical effects. When these bubbles collapse, they create extremely hot areas called hot spots which can generate reactive radicals useful for chemical reactions such as redox processes. The collapse also releases high pressure into the surrounding liquid, forming shockwaves that improve mixing and mass transfer. In addition, other associated physical effects such as acoustic streaming, microstreaming, microjet formation, and the appearance of microstreamers further contribute to improved fluid motion and process efficiency (Lamminen, 2004; Yusof *et al.*, 2016b).

Acoustic Streaming

Acoustic streaming refers to the steady fluid flow generated by the absorption of ultrasonic energy, and unlike cavitation, it does not require the collapse of bubbles to be initiated. This phenomenon can occur over relatively large spatial ranges, typically extending from a few centimeters to several tens of centimeters, and is often associated with flow velocities in the range of approximately 10 cm/s (Lamminen, 2004). Acoustic streaming tends to work more effectively in dead-end filtration systems compared to cross-flow setups (Kyllönen, Pirkonen and Nyström, 2005). The strength of acoustic streaming increases with both higher ultrasound frequencies and greater power input. Since it does not rely on violent cavitation events, acoustic streaming is particularly effective for removing loosely attached fouling layers composed of soluble or weakly bound particles. The back-and-forth movement of water molecules creates a localized velocity gradient near the membrane surface, which helps to dislodge and transport deposited particles away from the membrane interface (Lamminen, 2004).

Microstreamers

When ultrasonic waves from a transducer interact with waves reflected off a solid membrane surface, standing waves are produced. These flows are typically confined to just a few millimeters in range but move at speeds nearly approximately one order of magnitude higher than the average fluid flow (Qasim *et al.*, 2018). These microstreamers are generated by the motion of small cavitation bubbles, which follow curved, ribbon-like paths as they move toward antinodes, specific points in the ultrasonic field where acoustic pressure is highest (Lamminen, 2004). These antinodes are formed when ultrasound waves from a transducer interact with waves that bounce back from a solid surface, such as a membrane. According to the theory of Bjerknes forces, bubbles smaller than their natural resonance size are pulled toward these antinodes, while larger bubbles are drawn toward the opposite points in the wave field, known as nodes (Qasim *et al.*, 2018).

Microstreaming

Microstreaming occurs when cavitation bubbles oscillate under ultrasound, generating steady, localized fluid motion around them. This movement replaces nearby liquid molecules, creating shear forces, eddy currents (small circular flows), and flow speed variations that apply drag on surface-bound particles, aiding in their removal (Lamminen, 2004). The strength of microstreaming depends on ultrasound frequency. Lower frequencies produce larger bubble oscillations and stronger flow, while higher frequencies generate smaller bubbles and weaker effects. This flow is time-independent and results from pressure-driven oscillations that cause rapid fluid movement and shear near the bubble surface (Lamminen, 2004). The area influenced by microstreaming is generally confined to the bubble's diameter, approximately 1 to 100 micrometres depending on acoustic frequency and pressure, and is particularly effective at removing fouling materials when occurring near a solid surface (Verraes *et al.*, 2000; Collis *et al.*, 2010).

Microjets

When ultrasound is applied, cavitation bubbles tend to migrate toward the membrane surface and accumulate near the solid boundary. As this occurs, fluid motion around the bubble slows, resulting in a pressure difference and deformation of the bubble's shape. Once the pressure imbalance becomes significant, the bubble collapses and forms a micro-jet capable of dislodging fouling from the membrane surface (Wolloch and Kost, 2010; Qasim *et al.*, 2018). When cavitation bubbles collapse near solid surfaces or other nearby boundaries, their collapse becomes asymmetric. The side of the bubble facing away from the surface contracts faster than

the side facing the boundary, producing a narrow, high-velocity jet of liquid aimed directly at the surface. These micro-jets typically travel at speeds ranging from 100 to 200 m/s, and their impact area is limited to the approximate size of the bubble itself (Lamminen, 2004).

Shock Waves

Shockwaves play a significant role in reducing membrane fouling and are generated when cavitation bubbles collapse. This collapse produces zones of extremely high pressure, releasing shockwaves, often greater than 10 kbar that directed toward the membrane surface (Wolloch and Kost, 2010)

Heating

The conversion of ultrasonic energy into heat occurs as the wave is absorbed by the medium, leading to a rise in temperature, referred to as the thermal effect of ultrasound (Yao Jin, 2014).

2.7 Ultrasound Application in Membrane Fouling and Cleaning

In this section, the application of US is discussed as a promising strategy for both mitigating membrane fouling and enhancing membrane cleaning during filtration processes, as demonstrated by various studies. (S Muthukumaran *et al.*, 2005; Kyllönen *et al.*, 2006; Secondes *et al.*, 2014; Luján-Facundo *et al.*, 2016).

2.7.1 Enhancing Membrane Separation with US

Numerous studies have investigated the potential of US to enhance membrane permeation (Lennart and Ausländer, 1980; Band *et al.*, 1997; Chai, Kobayashi and Fujii, 1998). In a study employing dextran as a model foulant and PES membranes in a dead-end filtration cell, Cai, Zhao and Liang (2010) showed that low-frequency ultrasound (28 kHz and 45 kHz) reduced total fouling resistance (R_{tot}) and reversible fouling resistance (R_{rev}), resulting in a flux increase of 83% and 33%, respectively, at 0.4 bar TMP. This enhancement was attributed to the disruption of concentration polarization and cake layer by acoustic streaming and cavitation effect, while irreversible fouling was minimal due to the choice of foulant. Similarly, (2011) reported a reduction in both reversible and irreversible fouling during cross-flow UF of a clay suspension using hollow fiber polysulfone (PS) membranes. At a TMP of 175 kPa, the application of ultrasound at 40 kHz led to a 33% increase in flux, attributed to a significant decrease in fouling resistance.

In another study, Kobayashi, Chai and Fujii (1999) found that US effectively reduced solute concentration near the membrane surface, thereby enhancing water flux. Importantly, their results confirmed that ultrasonic treatment did not cause physical damage to the membrane surface. Cai, Wang and Liang (2012) further observed that ultrasound had minimal or negligible impact on solute adsorption and pore blockage in hollow fiber PS membranes, suggesting limited influence on the fouling mechanisms governed by internal membrane structure. The utility of ultrasound in removing cake layers and preventing pore blockage MF membranes was demonstrated by Muthukumaran *et al.* (2004), who highlighted its efficacy in maintaining membrane performance. In another study, Gao *et al.* (2012) investigated the role of ultrasound in controlling fouling in ceramic membranes used for surface water treatment in a cross-flow UF system. Their study demonstrated a significant improvement in normalized permeate flux from 0.21 in the absence of ultrasound to 0.70 when ultrasound was applied at a frequency of 20 kHz and power input of 16 W.

Kobayashi *et al.* (2003) examined the effect of ultrasound on membrane fouling during UF and MF of peptone and milk solutions. At an operating pressure of 60 kPa, they tested ultrasound frequencies of 28, 45, and 100 kHz. The 28 kHz frequency consistently showed the greatest reduction in fouling, indicating that lower frequencies are more effective for surface layer disruption without damaging the membrane. A follow-up study using a frequency range of 28–100 kHz at 23 W/cm² further confirmed that antifouling performance is strongly influenced by ultrasonic frequency. These results suggest that ultrasound, when optimally applied, can enhance membrane efficiency by minimizing fouling. Kyllönen *et al.* (2006) implemented a more advanced design for wastewater treatment, involving a rectangular cross-flow channel exposed to pulsed ultrasound. The transducer was positioned 1 cm above the membrane surface and operated for only a few seconds at a time. This approach improved filtration flux and reduced membrane fouling.

In another investigation, Chen, Weavers, and Walker (2006a) developed a cross-flow UF system equipped with ceramic membranes and an immersed ultrasonic transducer to address fouling caused by colloidal silica particles. Their experimental setup allowed direct coupling of acoustic energy into the filtration cell. When ultrasound was applied, permeate flux increased by up to 100%, indicating a substantial enhancement in performance. However, the beneficial effects diminished at higher TMP. In addition, when the distance between the transducer and the membrane was increased from 1.7 cm to 3.5 cm, the flux declined sharply. This finding highlights the importance of optimizing the transducer's placement relative to the membrane surface.

Simon *et al.* (2000) examined the influence of low-frequency ultrasound (20 kHz) on polymer filtration using polysulfone membranes in a dead-end Amicon ultrafiltration cell. Both pulsed and continuous ultrasound modes were tested, each resulting in increased flux without visible membrane damage. Their findings suggest that ultrasound helps to mix the fluid near the membrane and reduce the resistance to flow, which makes filtration more efficient.

Few studies have applied US directly to membrane modules. Mirzaie and Mohammadi (2012) converted a dead-end cell into a cross-flow setup for milk filtration, testing probe tips from 2 to 12.7 mm with 30 minutes of ultrasound. They found inconsistent coverage across the 40 mm membrane and poorly regulated flow conditions.

Hengl *et al.* (2014a) designed an ultrasound-assisted filtration device that used a metallic blade connected to a transducer. This was integrated into a cross-flow system with flat-sheet PES membranes. At 20 kHz and 20.5 W/cm², the device led to a significant improvement in flux without damaging the membrane. In the present study, a similar approach was undertaken, in which ultrasound was integrated into the membrane filtration.

2.7.2 Membrane Cleaning with US

Membrane fouling, a common challenge in pressure-driven membrane processes, is typically observed as a substantial reduction in permeate flux. This decline is primarily caused by the deposition and adsorption of retained solutes, particularly macromolecules, which block membrane pores and form a resistant layer on the surface. Such fouling significantly affects process efficiency, and effective cleaning strategies are essential for restoring membrane performance (Latt and Kobayashi, 2006). Traditional cleaning methods are widely used but may not always fully recover the original flux. In this context, US has emerged as a promising physical cleaning technique due to its ability to dislodge foulants via acoustic cavitation and microstreaming

effects. Compared to conventional methods, US-based cleaning has shown potential for enhanced flux recovery without causing membrane damage (Latt and Kobayashi, 2006).

Popović *et al.* (2010) reported that ultrasound was effective in cleaning ceramic membranes used for whey ultrafiltration. Kobayashi *et al.* (2003), studied MF using polysulfone and cellulose membranes fouled with 0.5 wt% peptone and 1 wt% milk solutions. In this study, the entire membrane unit was immersed in a water-filled ultrasonic bath. When ultrasound at 28 kHz was applied, the recovered permeate flux improved to approximately $4.5 \times 10^{-5} \text{ m}^3/\text{m}^2\cdot\text{s}$, compared to $1 \times 10^{-5} \text{ m}^3/\text{m}^2\cdot\text{s}$ achieved through water cleaning alone.

Muthukumaran *et al.* (2004) also examined ultrasound-assisted cleaning for flat-sheet polysulfone UF membranes used in whey processing. They applied ultrasound in combination with a surfactant solution and found that the cleaning was effective regardless of the sonication duration. The study used a 50 kHz ultrasonic bath, and results confirmed that acoustic cleaning could be further improved by either increasing the applied ultrasonic power or incorporating chemical additives like surfactants.

Ultrasonic cleaning has also been tested in off-line setups. Thombre *et al.* (2020) compared various cleaning methods for polyamide membranes fouled during nanofiltration of simulated petroleum refinery wastewater. Off-line ultrasonic cleaning at 24 kHz and 135 W achieved an 85% flux recovery, outperforming backwashing (58%) and chemical cleaning with 1.0 M NaOH (73%). The only drawback of off-line cleaning was that the system had to be stopped during the process, which can reduce overall productivity. Azami and Amirinejad (2019) also tested off-line ultrasound cleaning for polysulfone membranes used in dead-end ultrafiltration. They applied ultrasound at 20 kHz with a power of 63.7 W/cm² and achieved about 83% flux recovery. This supports the idea that ultrasound is a strong alternative to chemical cleaning, especially when on-line cleaning is not possible.

Beyond membrane filtration, the principle of ultrasonic cleaning has been explored in other industrial applications. For example, Korolev *et al.* (2011) developed a cleaning system to use ultrasonic cavitation to remove contaminants from roller bearing channels raceways.

2.7.3 Effective Parameters in US Performances

The performance of ultrasound in membrane processes depends on several important parameters, such as ultrasonic frequency, temperature, transmembrane pressure, feed concentration, and membrane material. These factors influence the effectiveness of cavitation, acoustic streaming, and overall fouling control.

Ultrasonic Frequency

One of the most influential factors in ultrasound-assisted membrane processes is the frequency of the ultrasonic waves. Low-frequency ultrasound tends to be more effective in enhancing both membrane cleaning and filtration performance. Frequencies in the range of 20 to 100 kHz are typically applied in studies focusing on membrane fouling reduction, with lower frequencies generally providing better results regardless of the membrane material or design (Wang *et al.*, 2014). Several researchers have demonstrated that applying low-frequency ultrasound improved the performance of ultrafiltration membranes used for whey treatment in cleaning and filtration (Shobha Muthukumaran *et al.*, 2005; Muthukumaran *et al.*, 2007).

Naddeo, Borea and Belgiorno (2015) evaluated the use of ultrasound in treating wastewater containing organic pollutants using polysulfone membranes. When the system was operated at

35 kHz (1.1 W/cm²), the removal of organic matter increased from 3% to 7% after four hours. Their comparison of 35 kHz and 130 kHz revealed that higher frequencies were more effective for improving oxidation. This enhancement was attributed to the formation of larger cavitation bubbles and more vigorous bubble collapse at lower frequencies, which promoted improved cleaning of the membrane surface.

Kyllönen *et al.* (2006) found that changing the ultrasound frequency had only a small effect on performance. In their study, using 200 kHz or switching from 200 kHz to 27 kHz at a constant input power of 200 W led to similar results. Similar observation was made by Cai *et al.* (2009) who looked at how ultrasound frequency affected reversible fouling.

Lamminen *et al.* (2004) found that lowering the ultrasonic frequency from above 1,000 kHz to below 10 kHz improved water permeability. Similarly, Heikkinen *et al.* (2017) showed that using 20 kHz nearly doubled the water flux by reducing concentration polarization. In both cases, higher frequencies had little effect. Comparable outcomes regarding flux improvement and cleaning efficiency were also reported by Luján-Facundo (2016).

Pressure

Ultrasound performance is affected by operating pressure. As pressure increases, cavitation weakens because bubble formation and collapse become harder. If cavitation is the main enhancement mechanism, ultrasound is more effective at low pressures. Ultrafiltration results showed only slight flux improvement with increased transmembrane pressure, suggesting that acoustic oscillations (not cavitation) were the dominant factor (Zhang *et al.*, 2019).

Chen, Weavers and Walker (2006b) focused on how ultrasound can help reduce membrane fouling during cross-flow ultrafiltration, using ceramic membranes and silica as the foulant. They placed the ultrasound probe in line with the membrane surface. Interestingly, they found that when the operating pressure was low, ultrasound significantly improved flux. However, as the pressure increased, the positive effect of ultrasound decreased. Specifically, the flux improvement dropped from 100% to 59% as pressure increased. This might be because higher pressure causes the liquid to move faster, which could interfere with how ultrasound interacts with the fouling layer on the membrane surface.

Similarly, Alventosa de Lara *et al.* (2014) tested US-assisted cleaning in a submerged UF membrane unit at TMPs of 0.5×10^5 , 1.5×10^5 , and 2.5×10^5 Pa, finding that cleaning was most effective at 1.1×10^5 Pa. Beyond this point, excessive turbulence and reduced surface interaction led to diminished performance. Raising TMP from 0.5×10^5 to 1.5×10^5 Pa enhanced cavitation and acoustic streaming, increasing turbulence and shear near the membrane. These forces helped remove attached particles. Kyllönen *et al.* (2006) investigated ultrasound-assisted filtration with transducers placed directly on the membrane module and observed that higher transmembrane pressures led to heavier fouling. This increased accumulation of contaminants made it more difficult for ultrasonic waves to effectively reach and clean the membrane surface.

Temperature

As the temperature increases, the liquid's viscosity and surface tension decrease, which typically allows cavitation bubbles to grow larger and last longer. These changes can enhance the impact of ultrasound on fouling removal (Ehsani, Doan and Lohi, 2021b). Chai, Kobayashi and Fujii (1999) studied the performance of ultrasound-assisted filtration using a peptone solution and found that increasing the temperature from 20 °C to 40 °C improved permeate flux. This improvement was mainly due to the reduced viscosity and increased back diffusion and

solubility of foulants at higher temperatures. Li *et al.* (2002) found that when cleaning micro-filtration membranes used for pulp and paper effluents, increasing the temperature from 23 °C to 40 °C weakened the cavitation intensity and reduced flux recovery. This suggests that there is an optimal temperature for ultrasonic cleaning. Wang *et al.* (2016) identified 30 °C as the optimal temperature for nanofiltration membrane cleaning for a solution containing inorganic materials. In their study, flux recovery improved between 15 °C and 30 °C but dropped sharply beyond that point.

Feed Concentration and Composition

The concentration of particles in the feed solution can directly affect cavitation and, in turn, US cleaning efficiency. A higher concentration of solids increases the viscosity and acoustic resistance of the liquid, making it harder for cavitation bubbles to form because a higher acoustic pressure is needed to break the cohesive forces between liquid molecules in order to generate cavitation, which is essential for ultrasound to have a cleaning or mixing effect during filtration (Kyllönen, Pirkonen and Nyström, 2005). In addition to concentration, particle size also affects fouling characteristics. Smaller particles tend to form more compact and resistant fouling layers, which increases membrane resistance and reduces flux (Ehsani, Doan and Lohi, 2021b).

Membrane Material

The way a membrane responds to ultrasound depends on both the material it's made from and its physical design. Common membrane materials include polymers and inorganic substances, and they are typically shaped as flat sheets, hollow fibers, or tubes. While ultrasound can help improve water flow and reduce clogging, it also has the potential to harm membranes that are too delicate. The tiny, powerful forces produced during ultrasound like shockwaves and microbubbles can deform soft polymer membrane surfaces. A major goal of this research was to better understand how different membranes hold up under ultrasound conditions (Zhang *et al.*, 2019).

2.8 Small angle X-ray scattering (SAXS)

Small-Angle X-ray Scattering (SAXS) is an advanced characterization technique used to investigate nanoscale structures in soft matter systems such as cellulose nanocrystals (CNCs). It is based on the elastic scattering of X-rays at very small angles, which allows for the detection of features ranging from 1 to 100 nm. In this method, a highly collimated X-ray beam interacts with the sample, and the scattered intensity is recorded as a function of the scattering angle. SAXS is particularly suitable for in situ and real-time studies because it is non-destructive and highly sensitive to variations in electron density (Yao Jin, 2014). The scheme of the process is shown in Figure 2.4.

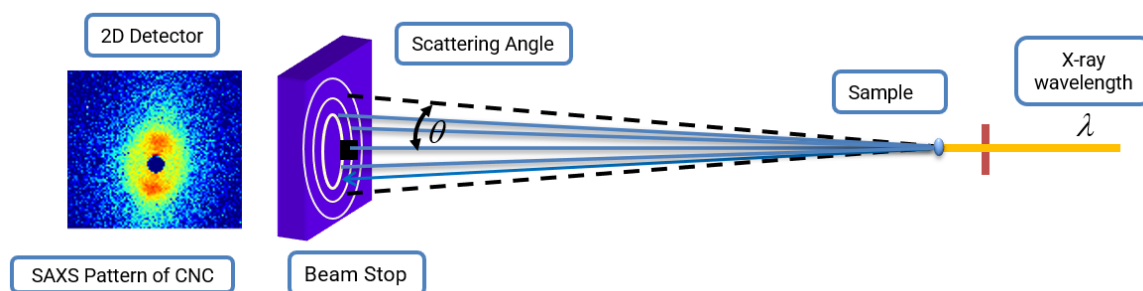


Figure 2.4 Scheme of the SAXS experiment procedure.

3 Materials and Methods

This chapter describes the materials, instruments, and experimental procedures used to investigate permeability, fouling behavior, and structural changes in CNC suspensions during ultrasound-assisted filtration with ENMs and PES membranes. In addition, it outlines the techniques used to characterize membrane performance including Scanning Electron Microscopy (SEM) and Small-Angle X-ray Scattering (SAXS).

3.1 Filtered Suspensions and Tested Membranes

CNC were obtained from the UMaine Development Center (University of Maine, USA) as a 10.8 wt% aqueous suspension. The dimensions of the CNCs were previously determined using electron microscopy and image analysis. The CNCs were 127.4 ± 34 nm in length, and 10.9 ± 2.6 nm in width (Mandin *et al.*, 2024). Two types of membranes were used in this study. The first was a commercial polyethersulfone membrane with a molecular weight cut-off (MWCO) of 100 kDa (Orelis environnement, France). The second consisted of electrospun nano, fibrous membranes (Politecnico di Torino, Italy). composed of styrene-butadiene rubber (SBR). These electrospun membranes were delivered in several batches with varying dimensions and thicknesses.

3.2 Ultrasound-assisted Filtration Set up

Ultrasound-assisted filtration was performed using a filtration cell made from transparent polycarbonate. To enable ultrasound delivery directly to the feed suspension, the cell was equipped with a titanium vibrating blade positioned 8 mm above the membrane surface. This blade was driven by a piezoelectric transducer connected to an ultrasonic generator, operating continuously at 20 kHz (Yao Jin, 2014). Figure 3.1 shows the filtration cell scheme of an ultrasonic-assisted membrane system. The standard feed channel measured 100 mm in length (tangential to flow) with a cross-sectional area of 4 mm $\times$ 8 mm. Three optical access windows (3 mm $\times$ 5.5 mm $\times$ 0.3 mm) were embedded along the feed compartment at intervals of 43 mm. Due to fabrication constraints, ENMs could not be produced in the dimensions to fit in the cell. Therefore, another cell was modified to accommodate smaller ENMs, reducing the feed channel length to 40 mm which is shown in Figure 3.2.

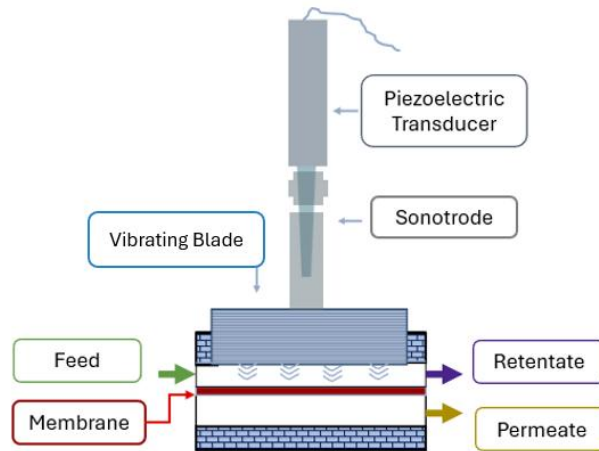


Figure 3.1 Scheme of an ultrasonic-assisted membrane filtration system.

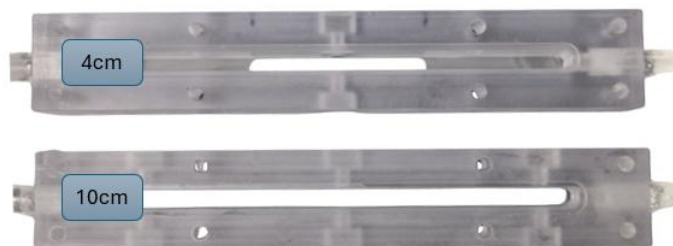


Figure 3.2 Two different feed channels used for ENMs and PES membranes.

The filtration setup consisted of a 5 L stainless steel feed tank (Millipore, Germany), from which the CNC suspension was circulated using a centrifugal pump (Mono, UK). The feed passed through a heat exchanger (Heto, Denmark) to maintain a constant temperature of either 20 °C or 25 °C, depending on the experiment. Ultrasound was applied through a 20 kHz ultrasonic generator (SODEVA, France) connected to a vibrating blade inside the filtration cell. System pressure was applied using compressed air and measured by pressure sensor. Flow rate was monitored using a rotameter (Brooks Instruments, USA). The filtered permeate was collected in a beaker placed on a balance (OHAUS, USA), which recorded the weight over time. Figure 3.3 shows the filtration with US process scheme.

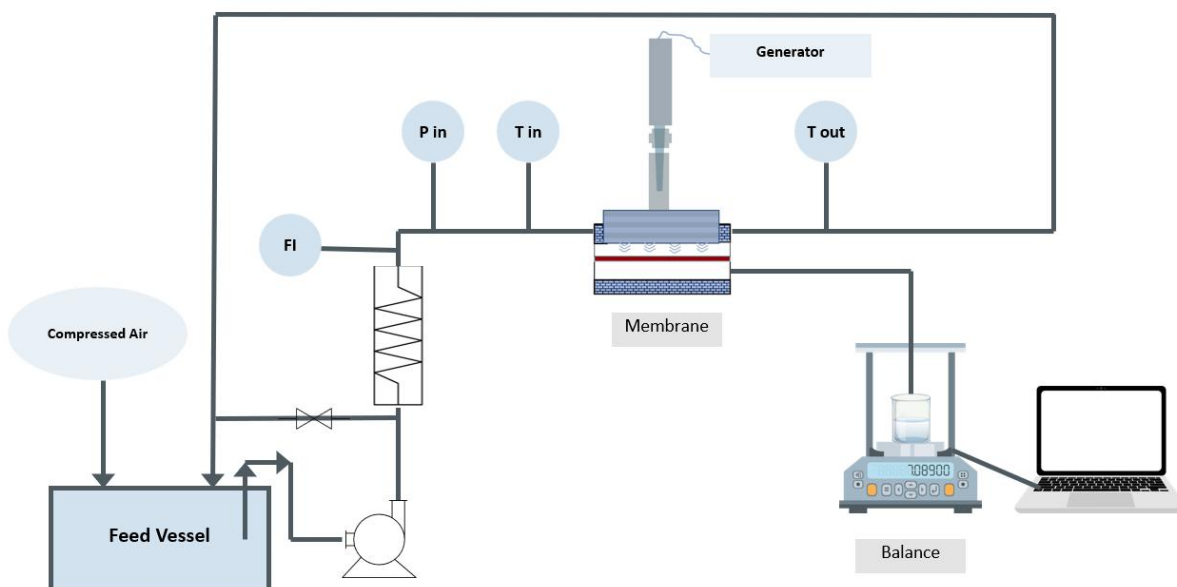


Figure 3.3 Scheme of the filtration system.

Due to fabrication limitations, the direct assessment of the fouling properties of the ESM membranes was not feasible at the outset. In an initial step, the fouling behavior of commercially available PES membranes was investigated to establish a reference. In a subsequent phase,

experiments were performed on the ESM membranes to enable a comparative evaluation. The following section details the experimental procedures applied to each membrane type.

3.3 Experimental Procedure for PES Membranes

3.3.1 Determination of Membrane Hydraulic Permeability

Before starting the experiment, the PES membrane sheets were carefully cut to match the size of the filtration cell (8 mm in width and 10 cm in length). A cleaning step was carried out to remove the glycerine preservative applied during manufacturing. This was done by putting the membranes first in deionized water and then add ethanol to it. Once cleaned, the membranes were placed inside the filtration unit. To ensure complete wetting, a small amount of distilled water was introduced to the cell and the pump using syringes. This helped to remove any air trapped in the system and ensured that the membrane surface was fully hydrated.

The membrane's hydraulic permeability was measured using deionized water at 25 °C. Three PES membranes with a molecular weight cut-off of 100 kDa were tested under different pressures (P) and crossflow rates (Q_v). The pressure was increased stepwise starting from 0.2 bar. At each pressure level, the system was allowed to stabilize, and then the permeate flux (J_v) was recorded. These flux values at steady state were plotted against the corresponding pressure values to create a J_v vs. P graph. The slope of the graph represents the membrane's hydraulic SUR estimated permeability (L_p), which was calculated using Equation (3.1). It should be noted that three distinct flow rates were employed in the experimental setup. While the transmembrane pressure (TMP) typically depends on both the inlet pressure and the pressure drop along the feed channel. Preliminary measurements indicated that even at the highest flow rate of 0.2 L/min, the pressure drop remained relatively low, at approximately 0.05 bar. Given the modest magnitude of this pressure loss and the configuration of the system, which closely approximates dead-end filtration, the inlet pressure was adopted as a first-order approximation of the TMP. This assumption enables a simplified yet sufficiently accurate evaluation of the system's filtration performance under the conditions investigated. The operation conditions for the PES water permeability tests are shown in Table 3.1.

Table 3.1 Operating conditions for water permeability of PES 100 kDa membranes.

No.	Membrane	P			Q_v (l/min)	T (°C)	A (m ²)
		0.5	0.9	1.2			
1	PES 100 kDa	0.5	0.9	1.2	0.05	25	0.0004
2	PES 100 kDa	0.5	0.9	1.2	0.15	25	0.0004
3	PES 100 kDa	0.5	0.9	1.2	0.20	25	0.0004

3.3.2 Determination of PES Membrane Stability under US

This part of the study aimed to evaluate the effect of US on the stability and performance of PES 100 kDa membranes. The experiments were carried out using distilled water at two different pressures (0.7 and 1.2 bar), with a constant crossflow velocity of 0.15 l/min at a temperature of 25 °C. Each test began by running the system until a stable water flux was achieved. After approximately 15 minutes of stable operation, ultrasound was applied in three separate intervals, using amplitudes of 40%, 60%, and 80%. These amplitudes correspond to different amounts of electrical power delivered to the ultrasound emitter. To allow comparison between conditions, the power was expressed as a power density (in W/cm²), calculated by dividing the electrical power by the surface area of the emitter. The emitter had a flat blade shape with dimensions of 0.3 cm × 10 cm, giving a surface area of 3 cm². In each case, the ultrasound was turned on and off in 2-minute cycles, while all other operating parameters were kept constant.

3.3.3 CNC Filtration Process under PES Membranes

To investigate the performance of PES membranes during CNC filtration and to evaluate their fouling behavior, four different experimental conditions were selected. Each membrane was tested under a specific combination of pressure and crossflow velocity, while maintaining a constant temperature of 25 °C. The membrane surface area used in all experiments was 4×10^{-4} m². The selected conditions are summarized in Table 3.2 and presented in Figure 3.4. This range of parameters was chosen to evaluate how different hydrodynamic conditions influence membrane fouling behavior and performances during CNC filtration.

Table 3.2 Operating conditions for PES membranes in CNC filtration.

No.	Membrane	P (bar)	Q _v (l/min)	T (°C)	A (m ²)
I	PES 100 kDa	1.2	0.20	25	0.0004
II	PES 100 kDa	1.2	0.05	25	0.0004
III	PES 100 kDa	0.5	0.20	25	0.0004
IV	PES 100 kDa	0.5	0.05	25	0.0004

Step 1: Permeability Testing with Distilled Water

As described in Section 3.4.1, the permeability of each PES membrane was measured using distilled water at 25 °C. The test was performed under the same conditions listed in Table 3.2, which reflects the operating parameters used later for CNC filtration. For all tests, the feed tank was filled with 1 L of distilled water.

Step 2: System Draining and Preparation for CNC Filtration

After completing the permeability tests, the feed tank was emptied to remove any remaining distilled water from the system. The emptying process was carried out using the same flow rate

as that used during permeability measurements and planned for the CNC filtration step. All tubing and the pump were carefully drained to ensure that no remaining distilled water could dilute or interfere with the upcoming CNC filtration experiments.

Step 3: CNC Suspension Preparation

The feed solution used for all filtration experiments was prepared from a concentrated cellulose nanocrystal stock suspension with a solid content of 10.8 wt%. To prepare the working solution, the concentrated CNC was diluted with distilled water to obtain a final concentration of 0.7 wt%. The solution was manually stirred to ensure that the CNC was fully dispersed and formed a homogeneous suspension

Step 4: Filtration of CNC with PES Membranes

After completing the initial membrane permeability and CNC baseline filtration tests, additional experiments were conducted to investigate the effect of ultrasound on membrane performance. The aim was to evaluate how different ultrasound amplitudes influence permeate flux and membrane fouling during CNC filtration. The suspension of CNC was added to feed tank and pump.

The filtration process was performed in a crossflow setup, where the CNC feed flowed tangentially across the membrane surface. The permeate (the filtered liquid) passed through the membrane and was collected from the outlet, while the retentate (containing CNC) was returned to the feed tank. This recirculation allowed the process to run continuously with the same feed volume. The flow rate was measured using a rotameter, and the pressure was monitored with a pressure sensor installed on the feed line. Pressure readings were displayed and recorded using the balance. The permeate was collected in a beaker placed on a digital balance connected to a computer. The balance recorded the weight of the permeate in real time, approximately every 0.1 seconds. This data was later used to calculate the permeate flux.

Once the system was running under stable operating conditions with 0.7 wt% CNC suspension, ultrasound was introduced at three different amplitudes: 40%, 60%, and 80%. Each amplitude level was applied for a duration of 30 minutes. The ultrasound was delivered in an on–off cycle to observe its influence in isolation. Specifically, after each 30-minute ultrasound application, the system was run for an additional 30 minutes without ultrasound under the same pressure and flow conditions. This alternating pattern helped to assess how membrane behavior changed with and without ultrasonic stimulation at each amplitude level. Figure 3.4 shows the CNC filtration process.

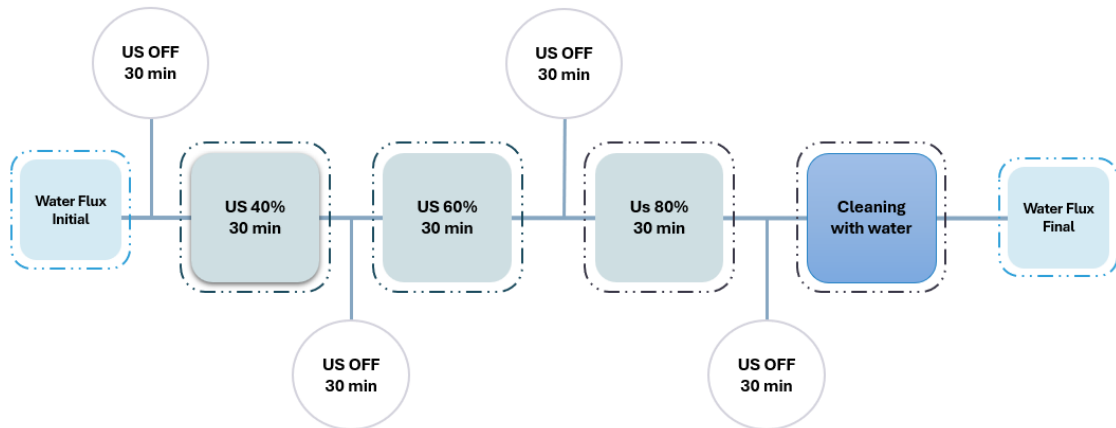


Figure 3.4 The filtration Process of CNC using PES membranes.

Step 5: Cleaning of the Membrane

After each CNC filtration experiment, the system was cleaned to remove any remaining CNC material from the system. The cleaning process also allowed for the recovery of the CNC suspension used during the experiment. To maintain consistency, the cleaning was performed using the same flow rate that was applied during the filtration step. This ensured that the hydrodynamic conditions remained comparable and helped to prevent any sudden pressure or flow fluctuations that might damage the membrane or affect its structure.

The cleaning process was done by flushing the system with distilled water, using the same crossflow setup as in the filtration step. The remaining CNC suspension (retentate) was collected and saved for future experiments. Once most of the CNC was removed from the membrane and tubing, the feed tank was washed with distilled water to clean out any leftover particles. The pump was also flushed to make sure no CNC material remained inside. This step was important to return the system to a clean state before taking the next step.

Step 6: Membrane Permeability after Filtration

At the end of each experiment, the membrane's permeability was measured again using the same method described in the step 1. As mentioned in Table 3.2, the tests were carried out with distilled water at 25 °C, using the same pressure and flow conditions applied during the initial permeability measurements. This step was conducted to assess whether any changes occurred in the membrane's performance due to CNC filtration, such as fouling, clogging, or structural alteration. By comparing the permeability values before and after filtration, the effect of the CNC suspension on membrane functionality could be evaluated.

3.4 Experimental Procedures for ENMs

Three batches of electrospun nanofibrous membranes were produced. During the initial training phase, fabrication conditions were progressively adjusted to improve membrane quality. The following procedure was applied to the optimized batch used for the experiments.

3.4.1 Initial Characterization and Stability Testing (Batch I)

This step aimed to evaluate the structural stability of the ENMs under US treatment. To do this, SEM analysis was performed on the membranes before and after ultrasound exposure to identify any changes in surface morphology or potential damage caused by the ultrasonic energy.

The ENMs were smaller in size (2.5 cm × 1 cm) than the filtration cell design (10 cm × 1 cm), which initially caused sealing issues and leakage. To resolve this, each ENM was placed on top of a PES 100 kDa membrane, which acted as a support layer and ensured proper sealing during testing. Ultrasound was applied at amplitudes of 40%, 60%, and 80%, each for 30 minutes, followed by a 30-minute period with US turned off. A constant crossflow velocity of 0.2 L/min was maintained, with no pressure applied.

3.4.2 ENMs Permeability Under pressure and Cross flow (Batch II)

After the initial characterization of the first batch of ENMs, it was determined that the membranes were too small to be tested in the existing filtration cell, which was designed for membranes with dimensions of 10 cm × 1 cm. As a result, no filtration experiments could be

conducted with Batch I, and a custom filtration cell with a shorter 4 cm feed channel was designed and fabricated to accommodate smaller membrane samples.

Once the new cell became available, Batch II membranes, provided by Politecnico di Torino, were tested. This batch included ENMs with dimensions of approximately 4 cm × 1 cm and 2 cm × 1 cm, fabricated under different electrospinning parameters to explore variations in membrane structure and performance.

The larger ENMs (4 cm × 1 cm) fit well in the modified cell and were tested directly without any PES support layer, as they could be properly sealed. However, the smaller membranes (2 cm × 1 cm) did not fit as securely, which led to sealing issues and the risk of leakage. To resolve this, these membranes were placed on top of PES support membranes with cuts on it. The support layer helped to both prevent leakage and enhance mechanical stability, which had previously been a limitation in unsupported tests with larger samples.

Following this, Batch III membranes were received from Politecnico di Torino. This batch included two large samples compared to the first two batches. These larger samples were tested directly in the new cell without PES support, as their size was compatible with the updated design. Some membranes from this batch were cut into 2 cm × 1 cm pieces to replicate the configuration of Batch II's smaller samples, allowing for comparative analysis. Table 3.3 summarizes eight experiments conducted to evaluate the permeability of ENMs under varying conditions. The membranes differed by type (Transparent - T or White - W), thickness, batch number, surface area, and support configuration.

Table 3.3 Experimental conditions for water permeability measurements of ENMs.

No.	Mem-brane	Batch	P (bar)	Qv (l/min)	T (°C)	A (m ²)	PES With Cuts	Thickness (cm)	Shape
1	ENM (T)	2	1.2	0.2	20	0.0004	No	0.009	
2	ENM (W)	2	1.2	0.2	20	0.0004	No	0.009	
3	ENM (W)	2	0.5	0.2	20	0.0004	No	0.009	
4	ENM (T)	2	0.5	0.2	20	0.0004	No	0.009	
5	ENM (W)	2	0.5	0.2	20	0.00008	Yes	0.006	
6	ENM (W)	3	0.5	0.2	20	0.00008	Yes	0.011	
7	ENM (w)	3	0.5	0.2	20	0.0004	No	0.011	
8	ENM (T)	3	0.5	0.2	20	0.0004	No	0.011	

3.4.3 CNC Filtration Process of ENMs

The CNC filtration experiments were conducted using a newly modified membrane cell designed for 4×1 cm membranes. However, the ENMs from Batch II in this size showed inhomogeneity and did not provide consistent results. To overcome this limitation, a support strategy was implemented by placing 2×1 cm ENM samples on a 10×1 cm PES membrane with

cuts. The PES served both as mechanical support and as a sealing layer to prevent leakage, while the cutouts allowed permeate flux to pass through only the ENM, ensuring that the measured permeability reflected the ENM alone.

Three membranes from Batch II were tested under identical conditions, following the same filtration protocol used for the PES membranes. Initial and final permeability values were measured to assess performance and fouling resistance. Table 3.4 summarizes the filtration conditions.

Table 3.4 Filtration conditions for CNC Tests on ENMs (Batch II) under US.

No.	Membrane	Batch	P (bar)	Q _v (L/min)	T (°C)	A (m ²)
I	SBR ENMs	2	0.5	0.20	20	0.00008
II	SBR ENMs	2	0.5	0.20	20	0.00008
III	SBR ENMs	2	0.5	0.20	20	0.00008

3.4.4 SEM Characterization of ENMs

In this section SEM (HIROX, Japan) was used to evaluate the surface structure and mechanical stability of ENMs from various batches. The membranes were examined both in their untreated (pristine) state and after exposure to US under conditions that simulated the filtration experiments. SEM imaging was conducted using a voltage of 15 kV on uncoated samples. Each membrane was observed at different magnifications, including ×60, ×1k, ×2k and ×4k to assess fiber morphology and detect potential structural changes.

To study the effects of operational conditions, some membranes were exposed to US at amplitudes of 40%, 60%, and 80%, each applied for 30 minutes, mimicking filtration conditions. Other samples were subjected to crossflow at 0.2 l/min and two pressure levels: 0.5 bar and 1.2 bar. SEM analysis was then performed on these treated samples to investigate compaction, and pore collapse.

3.5 Observed Parameters during the Filtration

3.5.1 Permeability Measurements

Membrane permeability was determined through pure water flux measurements. Permeate flux was calculated using the equation $J=V/A \cdot t$, where V is the volume of permeate collected, A is the effective membrane area, and t is the filtration time. Permeability (L_p) was then calculated using Equation (3.1).

$$L_p = \frac{J}{\Delta P} \quad (\text{Eq. 3.1})$$

3.5.2 Velocity Measurement and Reynolds Number

The velocity and Reynolds number of the four PES membranes I to IV were measured with Equation (3.2) and (3.3) respectively.

$$V = \frac{Q}{A} \quad (\text{Eq. 3.2})$$

Where Q is the volumetric flow rate (m³/s) and A is the cross-sectional area of the flow channel (m²).

The Reynolds number (Re) is a dimensionless parameter used to characterize fluid flow behavior and to distinguish between laminar and turbulent flow regimes.

$$Re = \frac{\rho V D_h}{\mu} \quad (\text{Eq. 3.3})$$

where ρ is the fluid density (kg/m³), V is the cross-flow velocity (m/s), D_h is the hydraulic diameter (m), and μ is the dynamic viscosity of the fluid (Pa·s). For all experiments, water at 25 °C was used as the feed fluid, with a density of 1000 kg/m³ and a dynamic viscosity of 0.000917 kg/(m·s) at 25 and 0.001036 kg/(m·s) at 20. The hydraulic diameter was calculated using $D_h = 4 (A/P)$ where A is the cross-sectional area and P is the wetted perimeter of the membrane channel, resulting in $D_h = 0.00533$ m. Table 3.5 shows the values of Re and V of four PES membranes.

Table 3.5 Velocity and Reynolds number measurement of the PES membranes.

No.	Membrane	Qv (l/min)	T (°C)	A _c (m ²)	V (m/s)	Re
1	PES 100 kDa (I, III)	0.20	25	0.000032	0.10	605.84
2	PES 100 kDa (II, IV)	0.05	25	0.000032	0.03	160.55
3	SBR ESM (I, II,III)	0.20	20	0.000032	0.10	536.25

3.5.3 Ultrasound Power and Enhancement Factor

The ultrasound power density (E), which can be calculated using Equation (3.4), is based on the generator power and the blade surface area in contact with the fluid.

$$E = \frac{P_{US}}{A_{US\ blade}} \quad (\text{Eq. 3.4})$$

where E is the ultrasound power density (W/cm^2), P_{us} is the ultrasound generator power (W), and $A_{\text{US blade}}$ is the blade surface area (cm^2). A constant area of 3 cm^2 was used, resulting in power densities of 4.0, 5.3, and $6.0 \text{ W}/\text{cm}^2$ for powers of 12 W, 16 W, and 18 W, respectively.

To quantify the effectiveness of ultrasound on filtration performance, the ultrasonic enhancement factor (UEF) was employed. It is defined as the ratio between the permeate flux obtained in the presence of ultrasound and the permeate flux obtained without ultrasound under the same operating conditions. It is defined by Equation (3.5) (Hengl *et al.*, 2014b):

$$UEF = \frac{J_{\text{us}}}{J_{\text{st.st}}} \quad (\text{Eq. 3.5})$$

where J_{us} is the average permeate flux during ultrasound on ($\text{L}/\text{m}^2 \cdot \text{h}$), and $J_{\text{st.st}}$ is the average permeate flux during ultrasound off ($\text{L}/\text{m}^2 \cdot \text{h}$).

3.5.4 Determination of the Fouling Resistances

Membrane resistance (R_m) represents the resistance to fluid flow through the membrane and is calculated using by Equation (3.6).

$$R_m = \frac{\mu}{L_p} \quad (\text{Eq. 3.6})$$

where μ is the dynamic viscosity of the fluid ($\text{Pa} \cdot \text{s}$), and L_p is the hydraulic permeability ($\text{m}^3/\text{m}^2/\text{Pa}/\text{s}$). The unit of membrane resistance is (m^{-1}).

To calculate the fouling resistance without US during filtration and with US in different amplitude measurement we use the formula in the Equation (3.7) and (3.8) respectively.

$$J_{\text{us}} = \frac{P_{\text{in}}}{(R_m + R_{\text{fouling}})\mu} \quad (\text{Eq. 3.7})$$

$$J_{\text{st.st}} = \frac{P_{\text{in}}}{(R_m + R_{\text{fouling us}})\mu} \quad (\text{Eq. 3.8})$$

where permeate fluxes are expressed in $\text{m}^3/\text{m}^2 \cdot \text{s}$, membrane resistance and fouling resistances are in m^{-1} , dynamic viscosity $\text{Pa} \cdot \text{s}$, pressure is given in Pa. To obtain the membrane resistance percentage the Equation (3.9) and (3.10) are used.

$$R_{\text{fouling}} (\%) = \left(\frac{R_{\text{fouling}}}{R_m + R_{\text{fouling}}} \right) \times 100 \quad (\text{Eq. 3.9})$$

$$R_{\text{fouling us}} (\%) = \left(\frac{R_{\text{fouling us}}}{R_m + R_{\text{fouling us}}} \right) \times 100 \quad (\text{Eq. 3.10})$$

3.6 Dead-End Filtration under SAXS Measurements

Small-Angle X-ray Scattering (SAXS) was employed to investigate the nanoscale structure and concentration profiles of CNC during filtration through ENMs and PES membranes. This technique allows precise detection of particle orientation and development of fouling layers. All experiments were carried out using a Xeuss 2.0 laboratory beamline from Xenocs equipped with a microfocus GeniX 3D Cu microsource and a Pilatus3 1M HPC detector from DECTRIS-Toulouse university. The filtration cell was mounted on a support, fixed on a precise motorized translation stage so that it can be readily moved in horizontal and vertical positions with respect to the X-ray beam in order to position the investigated channel in front of the beam. The sample to detector distance was 1.2195 m and the wavelength is $\lambda = 1.541 \text{ \AA}$ giving a q -range extending from $0.05 \text{ \AA}^{-1}$ to $2 \text{ \AA}^{-1}$. An acquisition time of one minute was used for each measurement to ensure enough statistical information on the detector. The beam was collimated to obtained $0.25 \times 0.25 \text{ mm}^2$ beam size on the sample.

3.6.1 Sample Preparation

In order to access to concentration profiles, a calibration curve was needed. CNC suspensions were prepared at concentrations ranging from 0.01 to 9 wt% (specifically: 0.01, 0.1, 1, 2, 3, 4, 5, 6, 7, 8, and 9 wt%). These samples were analyzed using SAXS to obtain different SAXS patterns.

3.6.2 SAXS Filtration Procedure

For the dead-end filtration experiments, a 6 wt% CNC suspension was prepared and used as the feed solution. Two membrane configurations were employed during the SAXS filtration experiments. For each, the measurements were performed through the middle window of the cell. The first setup used a 100 kDa PES membrane with an effective area of $4 \times 10^{-4} \text{ m}^2$. Prior to the actual filtration, a manual water flux test was performed to confirm the membrane's performance under the selected conditions.

In the second configuration, an electrospun nanofiber membrane from Batch II, cut to fit the modified filtration cell (approximately $4 \text{ cm} \times 1 \text{ cm}$), was tested. However, under the applied pressure, no measurable water flux was detected, indicating insufficient permeability and mechanical stability when used alone. To overcome this limitation, smaller ENM samples (approximately $2 \text{ cm} \times 1 \text{ cm}$) were placed on top of a PES support membrane with cuts. This adjustment helped improve sealing, supported the fragile ENMs mechanically, and enabled water passage through the membrane. The total active membrane area for this setup was approximately $8 \times 10^{-5} \text{ m}^2$. Both experiments were conducted in dead-end filtration mode under a constant pressure of 0.6 bar (with permeate at atmospheric pressure) and a temperature of 20°C for a total duration of 15 hours. This extended filtration time was selected to investigate the formation of a fouling layer.

During operation, a 6 wt% CNC suspension was continuously supplied to the feed side of the filtration cell. The system included a pressure sensor for real-time monitoring and an electronic balance to record the cumulative mass of permeate collected. This setup allowed SAXS measurements to be performed in situ, capturing the nanoscale structural evolution of the CNCs throughout the filtration process.

3.6.3 SAXS Data Analysis

A custom-designed filtration cell was integrated into the X-ray beamline to enable in situ SAXS measurements during dead-end filtration. When the focused X-ray beam interacts with the

suspended CNC particles, it generates a scattering pattern. By analyzing the scattering angle and intensity, it is possible to extract detailed information about the particle size, shape, and orientation.

Step 1: Calibration

To enable interpretation of the scattering data in terms of CNC concentration, a calibration curve was first developed. This was done by preparing CNC suspensions at known concentrations ranging from 1–9 wt%. For each sample, a 2D SAXS pattern was acquired and then processed through azimuthal integration to convert the image into a one-dimensional intensity profile $I(q)$, where q is the magnitude of the scattering vector. The scattering vector q was calculated using the Equation (3.11).

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (\text{Eq. 3.11})$$

where λ is the X-ray wavelength and θ is the scattering angle. From the $I(q)$ profile, the position of the primary scattering peak (q_{peak}) was identified, which corresponds to the characteristic spacing between CNC particles. The interparticle distance (d) was calculated using Equation (3.12).

$$d = \frac{2\pi}{q_{\text{peak}}} \quad (\text{Eq. 3.12})$$

These distances were plotted against their respective concentrations to create a calibration curve. This curve was later used to estimate local CNC concentrations in the fouled membrane by comparing unknown SAXS data to this reference. Figure 3.5 illustrates the resulting calibration curve obtained from CNC suspensions of known concentrations, showing the relationship between interparticle distance and concentration.

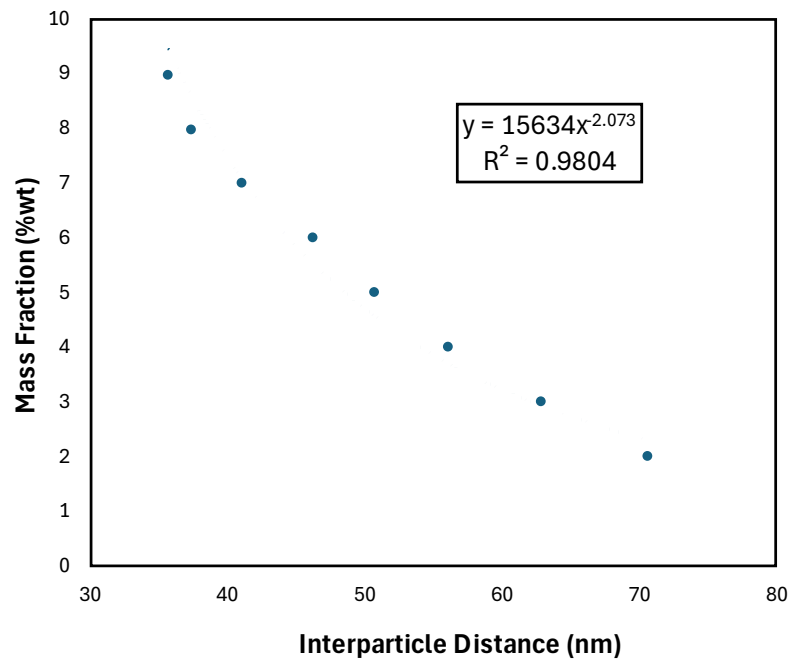


Figure 3.5 Calibration curve derived from SAXS measurements.

Step 2: Concentration Profile Determination

To examine the development of fouling and concentration polarization within the membrane module, SAXS measurements were carried out at multiple depths over time. The experiment spanned 15 hours, during which data were collected hourly. For each hour (from $t = 0$ to $t = 14$ h), measurements were taken along the vertical cross-section of the module at five positions, starting from the membrane surface and extending into the bulk solution, in 250 μm intervals. For the final timepoint ($t = 15$ h) the measurements were taken every 500 μm to capture a broader profile. At each position, a 2D scattering pattern was recorded.

Before analyzing the SAXS data, it was essential to remove all background signals that could interfere with the accurate interpretation of CNC scattering. The raw data contained not only scattering from the particles of CNCs but also unwanted contributions from the filtration cell, and the solvent (distilled water). If not properly subtracted, these background signals can distort the scattering profile, making it difficult to accurately determine particle spacing or concentration. In this study, the data provided for analysis had already undergone background subtraction.

In the next phase of the analysis, the SAXS data were processed using the open-source software SAXSutilities 0.2 (from ESRF), which is widely used for analyzing small-angle scattering data. The two-dimensional (2D) SAXS images collected from the module were converted into one-dimensional (1D) scattering intensity curves $I(q)$ through azimuthal integration. This technique transforms the circular scattering patterns into plots of intensity versus the scattering vector q , which makes it easier to analyze structural features of the sample. For every hourly timepoint, five $I(q)$ curves were generated, each corresponding to a different depth within the module (measured at 250 μm intervals). At each of these five positions, the value of q_{peak} was extracted. The interparticle distance (d) at each point was then calculated using Equation 3.

Once the interparticle distance (d) was determined from the SAXS data, it was used to estimate the local CNC concentration at each measurement point. This was done using the calibration curve developed from CNC suspensions of known concentrations (Figure 3.2). The curve relates interparticle distance (d) to CNC concentration and was fitted with an empirical equation derived from experimental SAXS measurements which is shown in Equation (3.13).

$$C_{\text{cnc}} = a \cdot d^b = 15634 \cdot d^{-2.73} \quad (\text{Eq. 3.13})$$

where C_{cnc} is the CNC concentration in wt%, d is the interparticle distance in nanometers, and a and b are constants obtained from curve fitting. Using this relationship, each measured d value from the membrane module was substituted into the equation to calculate the corresponding CNC concentration at that specific location. The calculated values were subsequently used to generate plots of CNC concentration profile.

Step3: 2D SAXS Scattering Patterns

In this step, the raw two-dimensional (2D) SAXS scattering images were analyzed to observe structural changes in CNC distribution over time. The data were processed using SAXSutilities 0.2. Although scattering data were collected for all timepoints during the 15-hour experiment, only patterns from $t = 0$, 2, and 4 hours are shown in the results to illustrate key structural changes.

3.6.4 Anisotropy of the CNC Structure

During filtration, different SAXS patterns were obtained at various time points and at different Z-distances from the membrane surface. These patterns appeared either elliptical or circular, depending on whether the CNC particles observed via SAXS were oriented or not. Figure 3.6 illustrates the relationship between particle orientation and the shape of the corresponding SAXS patterns. These measurements make it possible to determine the evolution of the structural organization of CNCs within the fouling layer during filtration.

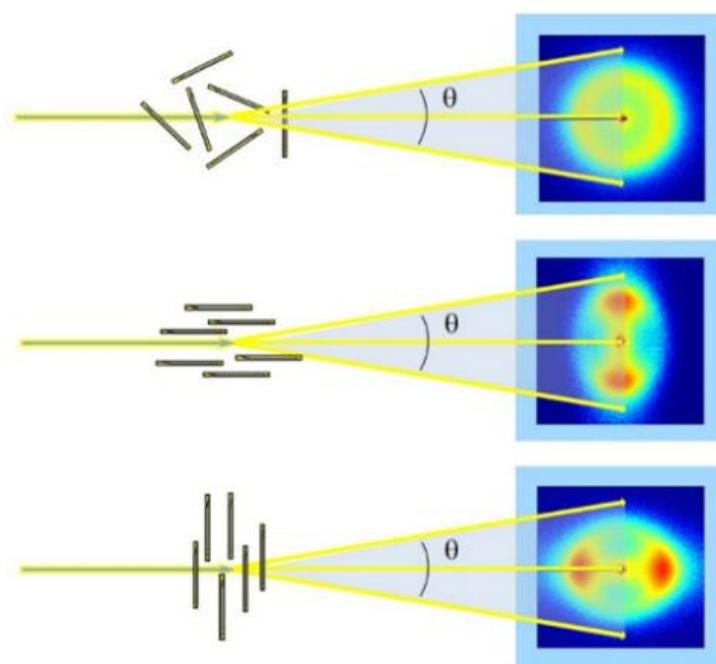


Figure 3.6 CNC structural organization during filtration.

4 Results & Discussions

This section presents the results of the experimental investigation into the permeability and fouling behaviour of PES membranes and ENMs. The membranes were evaluated both with and without the application of low-frequency ultrasound (20 kHz) during the filtration of CNC. The objective was to assess not only the filtration performances but also the structural stability of the membranes under sonication. Morphological characteristics were examined using SEM to identify surface-level changes induced by US. In addition, SAXS was employed to investigate the dead-end CNC filtration under non-sonicated conditions.

4.1 Permeability of PES Membranes

The permeability of PES membranes was first investigated under varying pressures and cross-flow velocities. Moreover, the effect of US at different power intensities was evaluated to determine its influence on membrane performance. Furthermore, permeability measurements before and after CNC filtration were compared to assess the impact of fouling and the application of US.

4.1.1 Water Permeability of PES Membranes

Water permeability was measured for three PES membranes with a 100 kDa MWCO under different cross-flow velocities and three pressures. The experimental setup was maintained at a constant temperature of 25 °C to ensure consistency across all tests. Figure 4.1 illustrates the relationship between the initial pressure (P) and water flux (Jp) for the membranes.

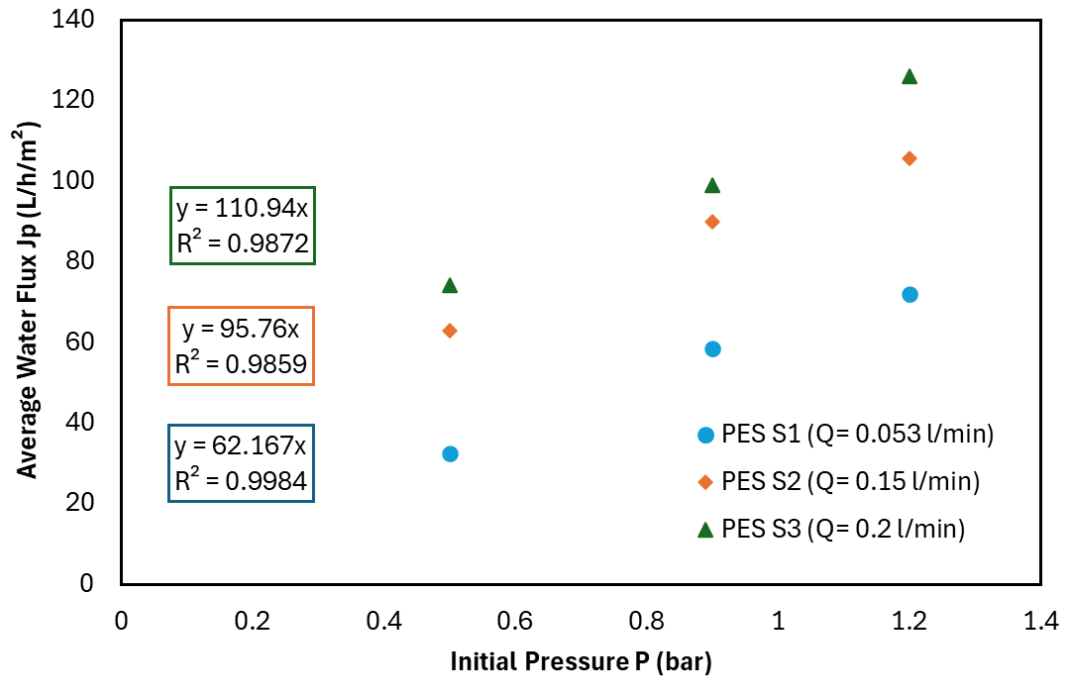


Figure 4.1 Average water flux versus initial pressure for three PES 100 kDa membranes

A clear positive linear correlation was observed in all three cases, demonstrating that water flux increased proportionally with pressure. This behaviour confirmed that higher pressure enhances the flux through pristine PES membranes by supplying a greater driving force for water permeation (Asif Khan *et al.*, 2023). Experiments were conducted in a closed cross-flow filtration cell at 25 °C, with pressures ranging from 0.5 to 1.2 bar. Each PES 100 kDa membrane was tested under a distinct cross-flow velocity: 0.05 L/min (PES S1), 0.15 L/min (PES S2), and 0.20 L/min (PES S3). A linear increase in water flux was observed for all membranes with increasing pressure, confirming Darcy's law behaviour. The slope of each trendline represents the membrane's hydraulic permeability, calculated as 62.17, 95.76, and 110.94 L·m⁻²·h⁻¹·bar⁻¹ for PES S1, S2, and S3 respectively. In this case, the measurements were performed in pure water, where no fouling occurs and the flow rate has no influence on the results. Therefore, the observed variations reflect only the experimental errors. Differences in permeability may also be due to slight variations in how the membranes were prepared or compacted during use. Additionally, the closed-cell design might have enhanced the effect of cross-flow by creating more stable and uniform flow conditions across the membrane.

4.1.2 Permeability of PES Membranes Under Ultrasound

To investigate the effect of US on membrane performance, PES 100 kDa membranes were tested with clean water at two pressures (0.7 and 1.2 bar) and a constant cross-flow velocity of 0.15 L/min. After a stable flux was recorded, ultrasound was applied in three intervals at amplitudes of 40%, 60%, and 80%, while all other conditions remained unchanged. Figure 4.2 shows the water flux over time during the entire experiment.

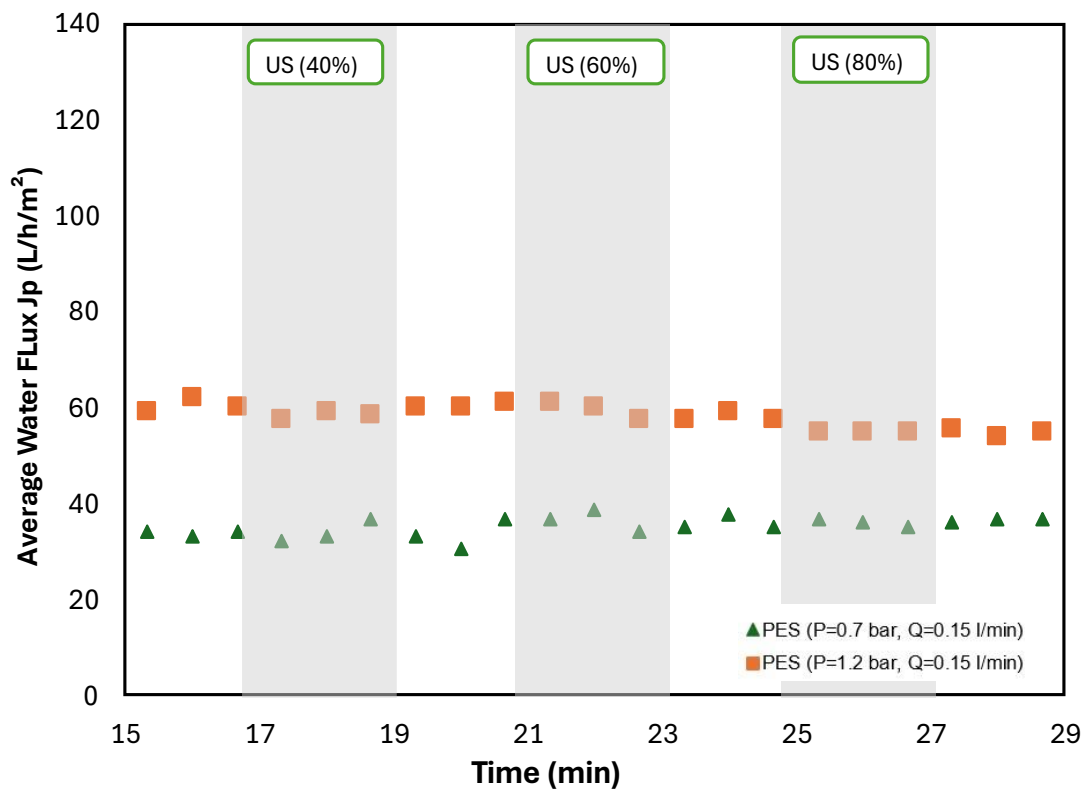


Figure 4.2 Average Water flux of PES membranes at 0.7 and 1.2 bar during ultrasound exposure at 40%, 60%, and 80% amplitudes.

The water flux remained relatively stable throughout the entire experiment, with no significant increase or fluctuation during or after ultrasound application. This indicates that the US amplitudes tested did not change the water transport through the membrane nor did they negatively affect the membrane structure. Overall, these results demonstrated that low to moderate ultrasound power levels (up to 80% amplitude) do not affect the permeability of PES membranes. Therefore, it was concluded that the membrane remains stable and performs reliably under these ultrasound conditions, making it suitable for further investigation in the filtration CNC in the next stage of the study.

4.2 Effect of US on CNC Filtration with PES Membranes

4.2.1 Flux Performance During CNC Filtration

To investigate the influence of operating parameters on ultrasound-assisted membrane performance, four PES 100 kDa membranes were tested under varying pressures and cross-flow velocities during CNC filtration, as detailed in Table 4.2. Results for two membranes are shown in Figure 4.3, which presents permeate flux over time, while data for the other two membranes are provided in the Appendix A. In both experiments, US was applied at amplitudes of 40%, 60%, and 80%, with each US-on period lasting 30 minutes followed by a 30-minute US-off period.

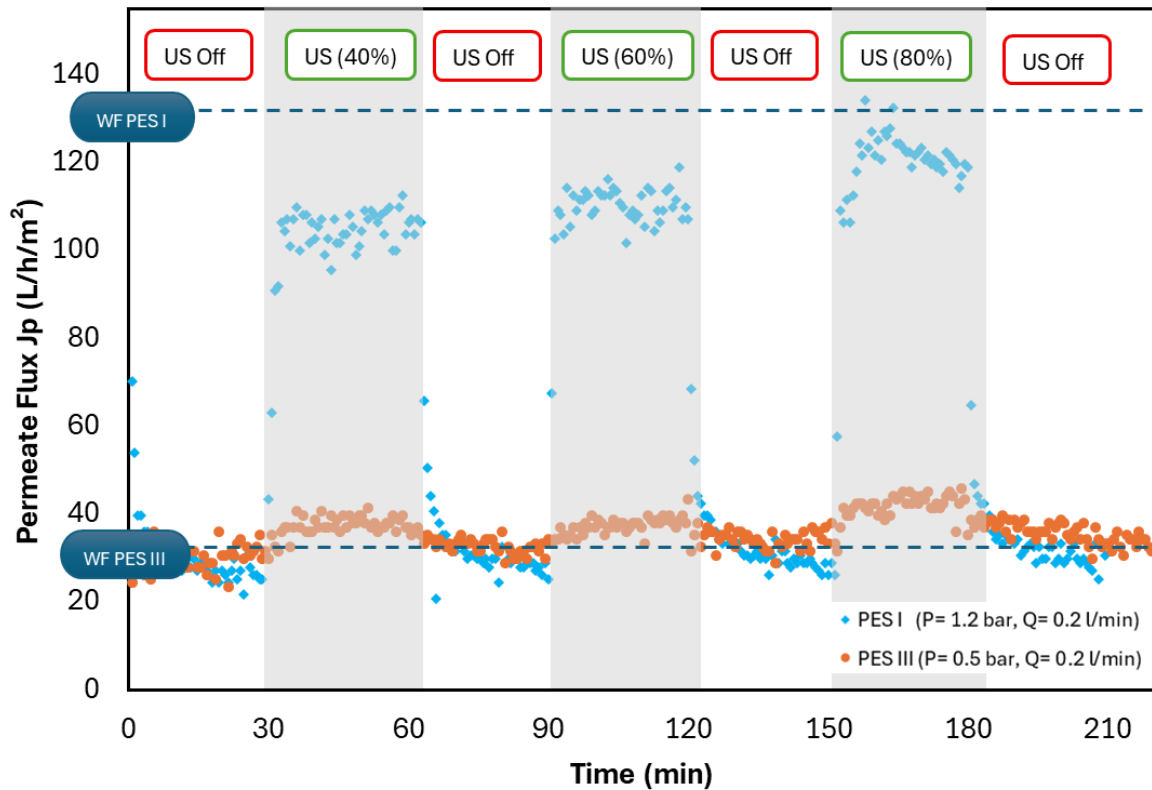


Figure 4.3 Permeate flux of PES membranes I and III during CNC filtration with ultrasound at 40%, 60%, and 80% amplitudes.

During CNC filtration, both PES I and PES III membranes showed a gradual decrease in water flux when US was turned off, indicating that fouling was building up on the membrane surface. Due to more accumulation, flux under higher pressure decreased more drastically (more than 80%). However, when US was applied at increasing power levels (40%, 60%, and 80%), the flux improved gradually. The application of ultrasound enhanced membrane performance by generating microbubbles, cavitation, or streaming effects that induced localized shear forces, effectively disrupting fouling buildup near the surface (Al-Hasani et al., 2022). For PES I, which operated at higher pressure (1.2 bar) and flow rate (0.2 L/min), ultrasound cleaning was strong enough to restore the flux close to its original clean water value, especially at 80% amplitude. In contrast, PES III, run at the same flow but lower pressure (0.5 bar), showed lower flux during ultrasound application but interestingly reached values higher than its initial clean water flux.

4.2.2 Water Permeability Performance before and after CNC Filtration

To evaluate the impact of CNC fouling and the effectiveness of US in preserving membrane performance, the pure water permeability of four PES 100 kDa membranes was measured before and after CNC filtration. Figure 4.4 presents the relationship between pressure and pure water flux for two membranes (PES I, PES III) before and after filtration.

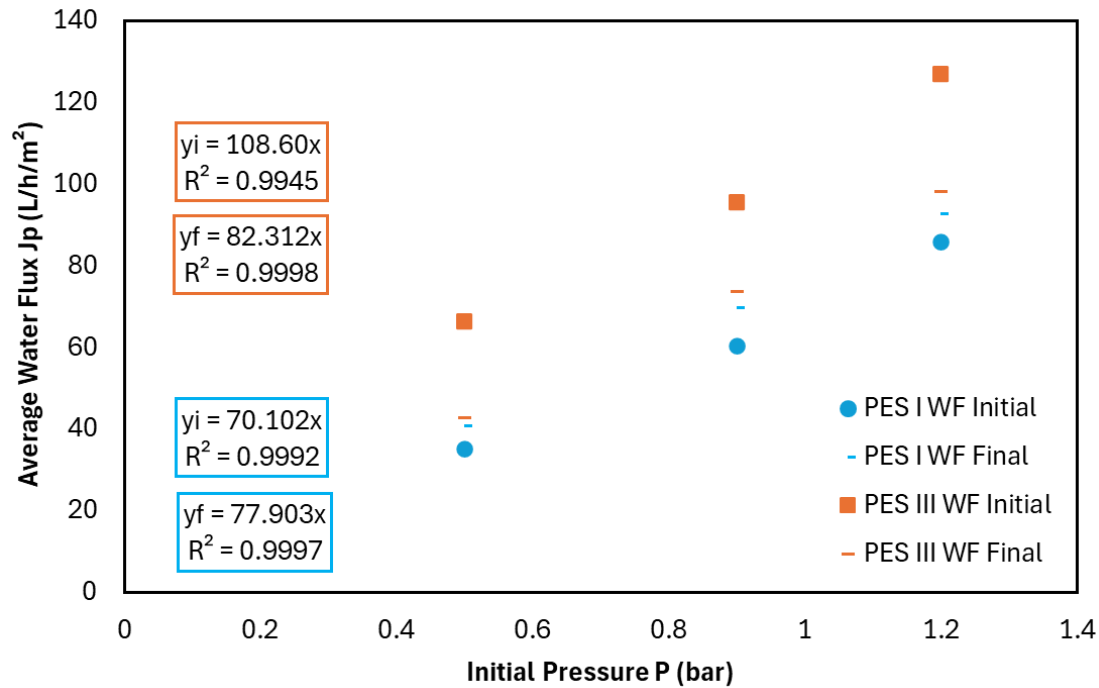


Figure 4.4 Average water flux as a function of pressure for PES I and III membranes before and after CNC filtration under US.

The average water flux for PES I increased linearly with pressure, showing an initial permeability of $108.60 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ before CNC filtration. After filtration, the flux decreased, and the permeability dropped to $82.31 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$, indicating fouling that reduced mass transport. On the other hand, PES III started at a lower initial permeability of $70.1 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$, but after CNC filtration, its permeability slightly increased to $77.9 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$. The permeability results for all experiments are presented in Figure 4.5.

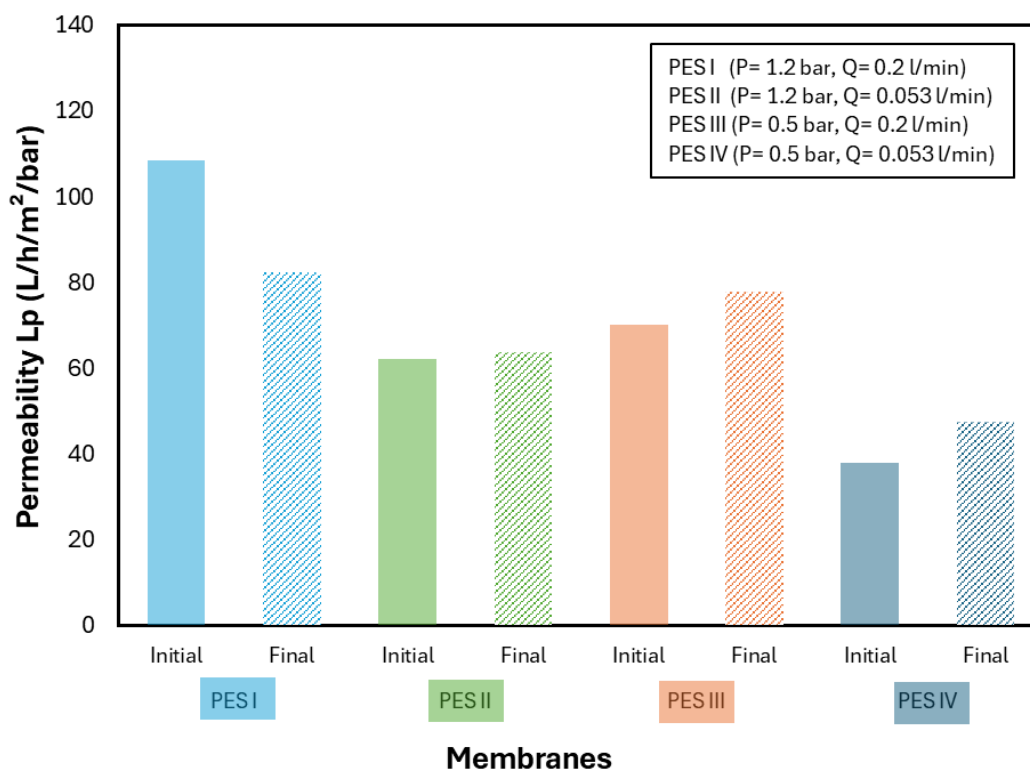


Figure 4.5 Permeability (L_p) of PES membranes measured before (initial) and after (final) CNC filtration with US.

The permeability results showed that for PES II, PES III, and PES IV, the membrane permeability after CNC filtration with US treatment was higher than the permeability measured before filtration. One likely reason for this is related to the cleaning and testing procedure. The residual foulants or deposits from previous CNC filtration experiments may have remained in the tubes or feed tank during the initial water flux measurement, lowering the initial permeability recorded for the subsequent experiment. Another possible explanation is that ultrasound treatment caused slight pore expansion, increasing membrane permeability. In contrast, PES I, with higher pressure and flow rates, showed a notable decline in permeability after filtration. This outcome was likely due to the development of more denser and compact fouling layer that US was unable to fully eliminate. Finally, only water cleaning was performed, and its effectiveness may have varied slightly between experiments. Chemical cleaning might have been more efficient in restoring membrane performance.

4.2.3 Fouling behaviour of PES Membranes

The fouling resistance of four PES membranes (PES I–IV) was evaluated with and without US at amplitudes of 40%, 60%, and 80%, as shown in Figure 4.6.

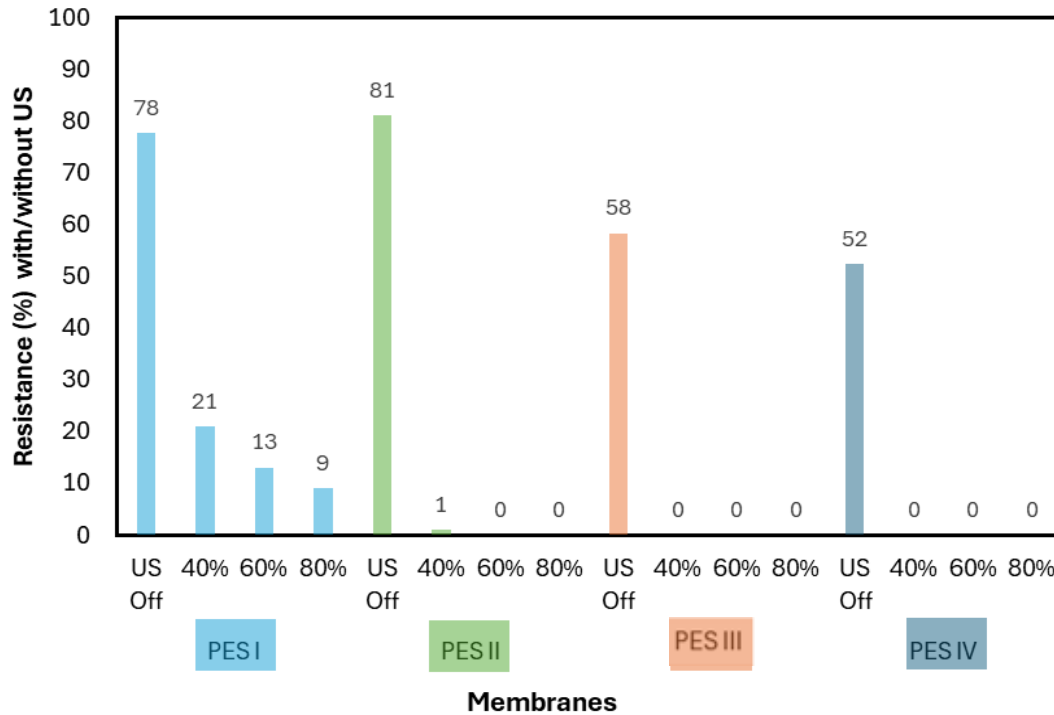


Figure 4.6 Fouling resistance of PES membranes during CNC filtration with and without US

The application of ultrasound proved to be highly effective, significantly enhancing filtration performance and reducing fouling across all tested membranes. US consistently improved permeability and nearly eliminated fouling, especially at higher amplitudes. Without US, all membranes showed significant fouling resistance. Upon applying US, fouling resistance decreased dramatically for all membranes, with near-complete fouling mitigation observed at 60% and 80% US amplitudes for PES II, PES III, and PES IV. PES I also experienced a substantial reduction in resistance, although some fouling persisted. These findings demonstrate that ultrasound effectively disrupts foulant layers, with higher amplitudes providing improved fouling control. This observation aligns with the study of Qasim *et al.* (2018) and Yao Jin (2014) which reported that increasing ultrasound power intensity enhances flux performance up to an optimal threshold, beyond which further increases do not lead to significant gains. Differences among the membranes suggest that under US, membranes operated at lower pressure (PES III and PES IV, 0.5 bar) show better permeability compared to those operated at higher pressure (PES I and PES II, 1.2 bar). This suggests that lower pressure, when combined with US, is more effective in limiting fouling and preserving membrane performance. The results shows that US enhances filtration, but its impact is even more profound under lower pressure conditions. These results demonstrate that while US significantly improves filtration efficiency, its effectiveness is enhanced under low-pressure and high-flow conditions. The optimal CNC filtration performance is a TMP of 0.5 bar and a flow rate of 0.2 L/min.

4.2.4 US Enhancement Factor effect on PES membranes During CNC Filtration

The ultrasound enhancement factor quantifies the improvement in water flux due to ultrasound treatment across different filtration conditions. Figure 4.7 presents the enhancement factor for different PES membranes at multiple ultrasound power levels.

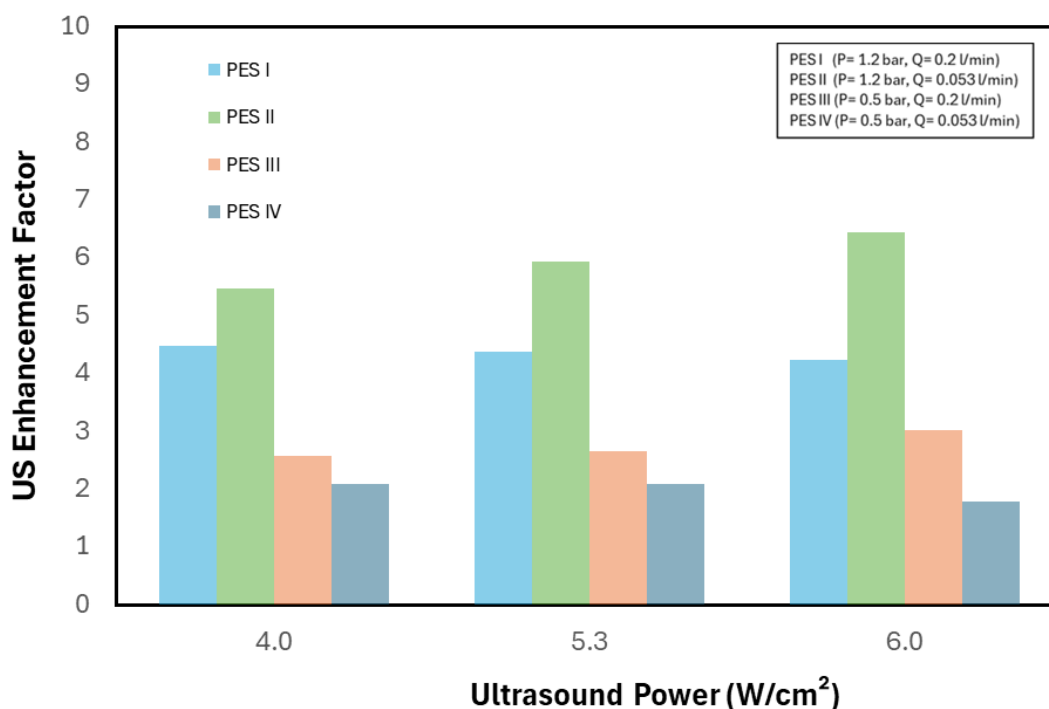


Figure 4.7 US enhancement factor for PES membranes at different US power levels.

Among all membranes, PES III (low pressure, high flow) showed the most stable and consistent performance, with minimal fouling and moderate enhancement under US, indicating that favourable hydrodynamic conditions reduce reliance on US. PES I and PES IV showed moderate fouling and responded well to US. Surprisingly, PES II (high pressure, low flow) exhibited the highest enhancement factor, with flux temporarily exceeding the initial pure water value during US. Since the final water permeability returned to baseline, this extreme enhancement is likely due to temporary effects such as fouling layer disruption or local mixing. However, the fact that flux exceeds the clean value is unusual and may involve non-steady-state transport or experimental errors. Further investigation is needed to fully understand this behavior. To better understand the fouling behavior in PES membranes, SAXS measurements under these specific filtration conditions could offer valuable insight into the structural organization and dynamics of the fouling layer. This would be particularly useful in clarifying how ultrasound influences CNC alignment, compaction, or disruption near the membrane surface.

4.3 Characterization of PES Membrane Filtration using SAXS

This section presents the structural analysis of PES membranes using Small-Angle X-ray Scattering (SAXS). Both the scattering pattern and the concentration profiles were examined to evaluate possible changes in the internal structure inside the deposit during dead-end filtration.

4.3.1 Concentration Profile

The concentration distribution of CNC near the PES membrane surface plays a crucial role in membrane fouling and filtration efficiency. Figure 4.8 presents the mass fraction profiles of CNC at various distances from the membrane surface during 15 hours of dead-end filtration at 0.6 bar with a 6 wt% CNC feed solution.

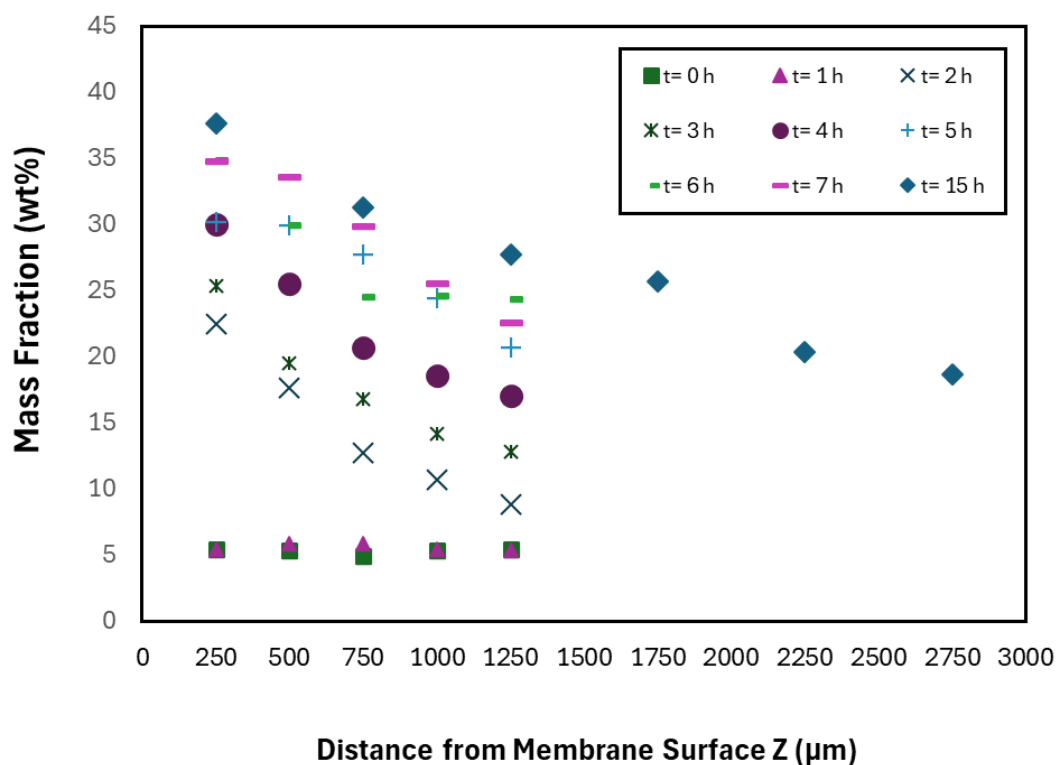


Figure 4.8 Concentration profile of CNC at various distances from the PES membrane surface over 15 hours of dead-end filtration.

Initially, CNC concentration was uniform throughout the cell, indicating little accumulation. After 3 hours, CNC began to accumulate near the membrane surface, reaching over 30 wt% by 6 to 7 hours. The concentration near the membrane stabilized after 7 hours, suggesting the formation of a steady fouling layer. This stabilization occurred because, in dead-end filtration, as the fouling layer thickens, it creates additional resistance that slows further particle buildup. Compaction of the fouling layer may also limit further accumulation by restricting particle transport to the membrane surface. This steady layer may increase membrane resistance and reduce filtration efficiency.

4.3.2 SAXS Scattering Patterns

The 2D SAXS scattering patterns shown in Figure 4.9 provide insight into the structural evolution of CNC across the filtration cell over time and at varying distances from the membrane surface. The color scale represents the intensity of X-ray scattering, where red and yellow indicate regions of higher scattering intensity, corresponding to higher local CNC concentration.

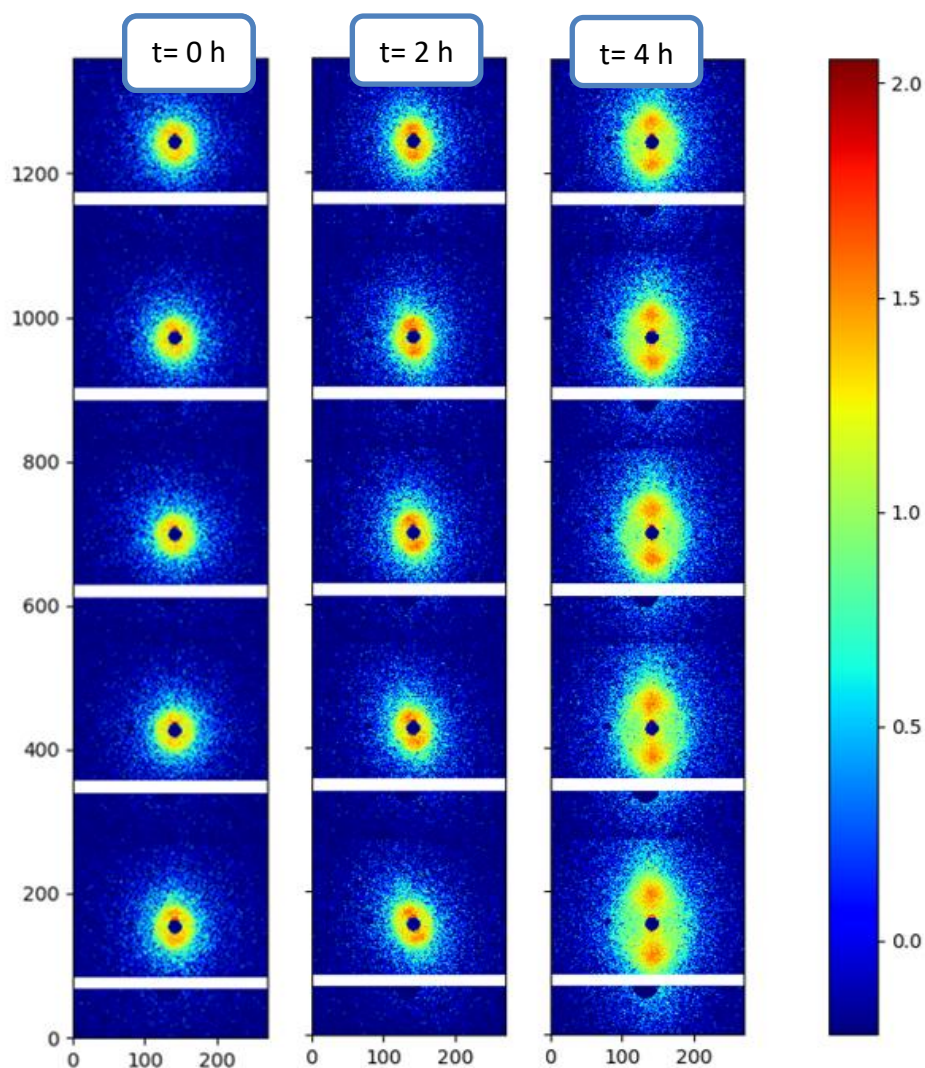


Figure 4.9 Two-dimensional SAXS scattering patterns of CNC measured at different distances from the membrane surface during filtration at 0, 2, and 4 hours.

At low concentrations, CNC particles are in an isotropic phase, which means they are randomly distributed and oriented in the suspension. In this state, there is no specific order, the particles float around freely, and the material looks the same in all directions. As the concentration increases, the CNCs begin to interact more closely. They start to align and arrange themselves into organized layers, with each layer slightly twisted compared to the one below it. This creates a helical or spiral structure, known as a chiral nematic phase (also called cholesteric phase) (Yao Jin, 2014).

As shown in Figure 4.8, at the initial time point (0 hours), the scattering patterns were isotropic and uniform across all measured depths, indicating a homogeneous distribution of CNC particles with random orientation. After 2 hours, the patterns near the membrane surface displayed slight anisotropy, reflecting the CNC accumulation and partial alignment driven by filtration forces. After 4 hours, this anisotropy of the patterns became more clear near the membrane, indicating the formation of a more concentrated and more ordered CNC layer.

4.4 Permeability of ENMs Membranes

This section presents an investigation into the permeability of ENMs from three different batches sourced from Italy. The new filtration cell was redesigned to accommodate membranes sized 4 cm × 1 cm. However, since some available ENM samples were smaller and thinner, ranging from 2 cm × 1 cm, a supporting layer of PES membrane with cuts was introduced underneath to prevent leakage and ensure proper sealing within the cell. The PES membrane also served to minimize additional resistance; the cuts allowed water to pass freely so that all flux measurements reported here correspond to the ENMs placed on top. All tests were conducted at a controlled temperature of 20 °C and a cross-flow velocity of 0.2 L/min. The experimental conditions and resulting permeability values are summarized in Table 4.1.

Table 4.1 Experimental conditions and water permeability (L_p) of ENMS from three batches.

Exp No.	Membrane	Batch	P (bar)	A (m ²)	PES Support	Thickness (cm)	Lp L·m ⁻² ·h ⁻¹ ·bar ⁻¹
1	ENM (T)	2	1.2	0.0004	No	0.009	No
2	ENM (W)	2	1.2	0.0004	No	0.009	No
3	ENM (W)	2	0.5	0.0004	No	0.009	No
4	ENM (T)	2	0.5	0.0004	No	0.009	No
5	ENM (W)	2	0.5	0.00008	Yes	0.006	69.99
6	ENM (W)	3	0.5	0.00008	Yes	0.011	45.50
7	ENM (w)	3	0.5	0.0004	No	0.011	50.40
8	ENM (T)	3	0.5	0.0004	No	0.011	No

The membrane samples evaluated originate from three different batches and exhibit notable variation in size, thickness, and appearance. Several larger samples (~4 cm × 1 cm) from batch 2, identified as Experiments 1, 2, and 3, appeared either white or partially transparent. Initial permeability tests for these membranes were conducted at a transmembrane pressure of 1.2 bar (Experiments 1 and 2). No stable flux was recorded. The permeate flux fluctuated near zero, with initial brief fluxes rapidly declining to values close to zero, indicating unstable and negligible permeability. This behavior was likely due to membrane compaction, or structural failure caused by the membranes' inability to withstand high pressure, resulting in pore blockage or breakage.

The pressure was reduced to 0.5 bar in Experiments 3 and 4 to reduce stress on the membranes. However, even at this lower pressure, the transparent and white membranes from batch 2

without PES support could not maintain steady water flux. The flux values went up and down near zero and eventually dropped, showing that these unsupported membranes were too fragile to keep their pores open during filtration. Their thin structure and uneven fiber distribution likely caused them to collapse or deform. Without a strong backing, the membranes could not keep a stable flow path, leading to no permeability.

In Experiment 5, white ENMs from batch 2 were placed on a PES support membrane with cuts to stop leakage and hold the fragile ENM in place. Running water at 0.5 bar produced a steady flux, corresponding to a permeability of $69.99 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$. Since the PES with cuts offers no flow resistance, all the measured permeate must pass through the ENM itself. The PES layer also prevents the ENM from collapsing under pressure and the cross flow. This simple combination delivered consistent water permeability under these test conditions.

The third batch's white ENMs, at a thickness of 0.011 cm, achieved measurable permeability both with and without PES support. In Experiment 6, using PES as a support layer, the permeability was measured to be $45.50 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$. Remarkably, the identical white membrane tested unsupported (Exp. 7) delivered a close result of $50.40 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$, demonstrating that the third batch's increased thickness is sufficient to maintain stable under 0.5 bar. Moreover, the effective use of the PES-with-cuts backing method in Experiment 6 highlights its practical benefit as a low-resistance support. This approach not only ensured stable permeability measurements but also prevented structural deformation of fragile membranes under pressure.

4.5 Effect of US on CNC Filtration with ENMs

This section explores how ultrasound affects CNC filtration using electrospun nanofiber membranes. It covers flux behavior, fouling, changes in water permeability, and the ultrasound enhancement factor, to evaluate the overall impact of ultrasound on membrane performance.

4.5.1 Flux of ENMs under US

The application of US had a noticeable impact on the permeate flux through the ENMs over time. Filtration experiments were conducted at a constant operating pressure of 0.5 bar and a cross-flow velocity of 0.2 L/min, using three different ENM membranes. Ultrasound was applied in three stages, with amplitude levels set at 40%, 60%, and 80%, respectively. Each stage lasted for 30 minutes and was followed by a 30-minute interval without ultrasound. The changes in permeate flux observed during these stages are presented in Figure 4.10. Additional results from Experiments 1 and 2, including flux performance data, are provided in Appendix B.

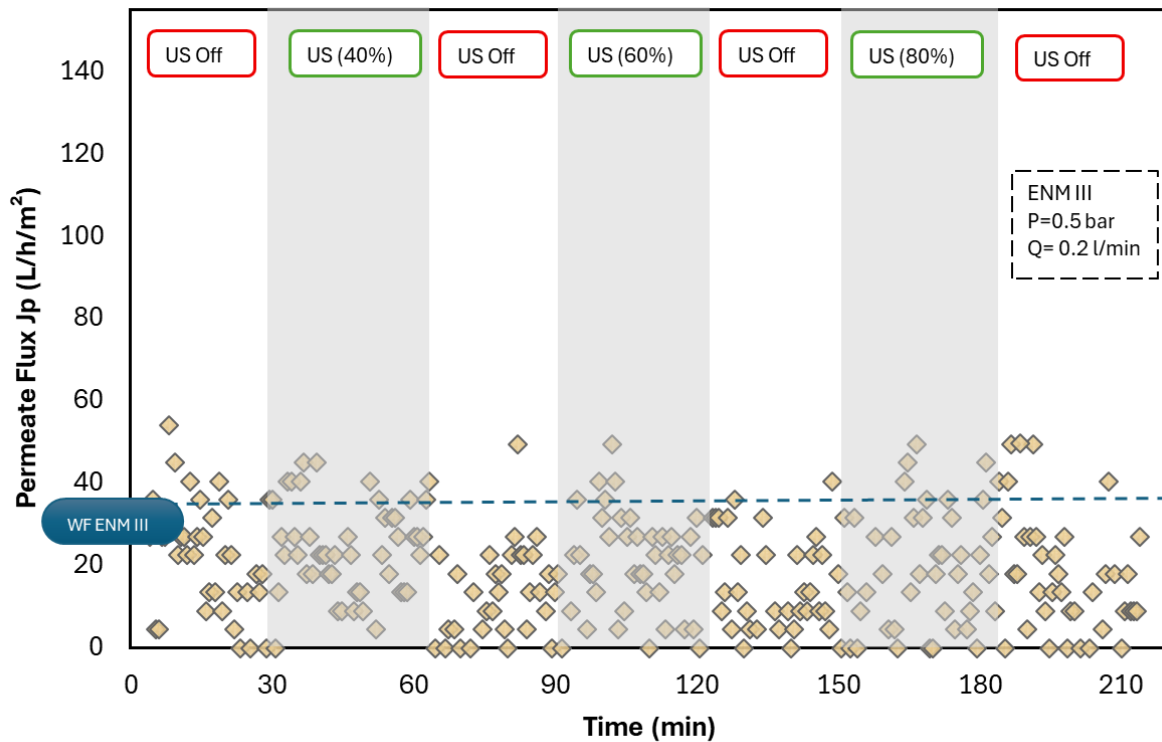


Figure 4.10 The permeate flux of ENM III during filtration under US.

Over the course of the experiment, a gradual decrease in permeate flux was observed, particularly during the initial phase of CNC filtration. This trend indicates the early development of membrane fouling, likely due to the accumulation of CNC at or near the membrane surface. While the application of US resulted in slight and short-term improvements in flux, increasing the amplitude from 40% to 80% did not lead to a consistent enhancement in overall performance. Interestingly, during certain phases of the experiment, particularly under ultrasound at higher amplitudes, the permeate flux not only recovered to the level of the initial pure water flux but, in some instances, even exceeded it.

This result suggests that ultrasound was able to temporarily clean the membrane surface by removing fouling caused by CNC particles. However, the improvement in flux was not consistent or long-lasting. Because the ultrasound was applied only for short periods, there were times when it was turned off. During these off-periods, CNC particles could enter the membrane pores. As a result, the positive effects of ultrasound during the "on" times gradually disappeared once the ultrasound stopped. This explains why the flux improved temporarily but did not stay high throughout the experiment.

4.5.2 Permeability of ENMs before and after CNC Filtration

Assessing membrane permeability before and after CNC filtration is essential for understanding the extent of fouling and whether it is reversible. While permeate flux measurements during filtration offer real-time insights into membrane performance, they may not fully reflect internal or irreversible fouling that develops gradually. In contrast, comparing the pure water permeability before and after the filtration process provides a more comprehensive evaluation of

membrane performance. The permeability results for all three membranes are summarized in Figure 4.11, which presents a comparison of initial and final water permeability, before and after US.

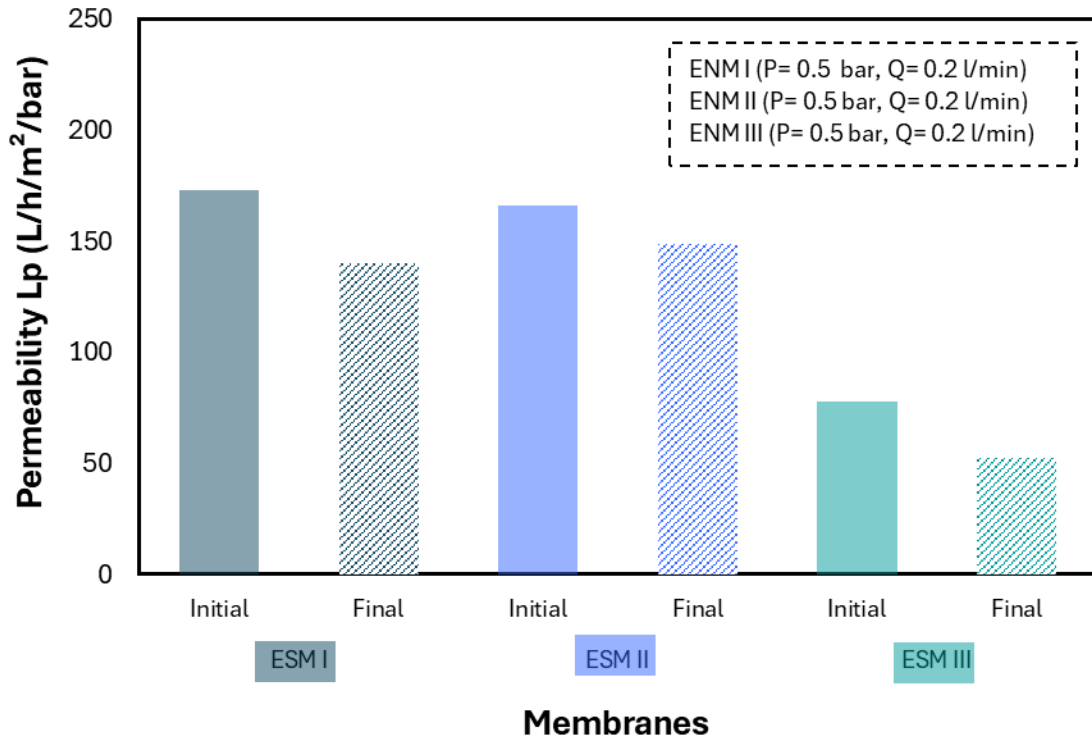


Figure 4.11 Initial and final pure water permeability of ENM I, ENM II, and ENM III before and after CNC filtration under US.

Among the three membranes tested, ENM III was the only one that showed permeate flux values during filtration that recovered to, and occasionally exceeded, its initial water flux. This indicated that ultrasound was able to temporarily restore surface conditions and reduce resistance to flow. However, its water permeability decreased significantly from 77.90 to 52.62 L/h·m²·bar. This confirms that internal fouling occurred despite the apparent improvement in flux, likely due to CNC particles entering or blocking membrane pores during ultrasound-off periods.

On the other hand, ENM I and ENM II started with higher initial water permeability values (173.14 and 165.82 L/h·m²·bar, respectively), but during CNC filtration, their flux never reached the level of the initial pure water flux. This means that fouling started early and remained throughout the process. Even though ultrasound was applied at increasing amplitudes (40%, 60%, and 80%), it did not lead to a clear improvement in flux or prevented fouling in either membrane. After filtration, the final water permeability of ENM I and ENM II dropped to 140.29 and 148.63 L/h·m²·bar respectively. These results suggest that the fouling in these two membranes was mainly on the surface and reversible.

Although ENM I, ENM II, and ENM III were produced from the same material using the same electrospinning process, their initial water permeability values were different. This difference

could be due to variations in membrane structure which may have occurred during fabrication. Factors like electrospinning duration, or solution flow rate might have caused these structural differences.

4.5.3 Fouling behaviour of ENMs Membranes

One way to evaluate the extent of fouling is by measuring the filtration resistance caused by foulant accumulation. Figure 4.12 shows the calculated resistance values for ENM I, ENM II, and ENM III during CNC filtration, both without US and with different US amplitudes (40%, 60%, and 80%).

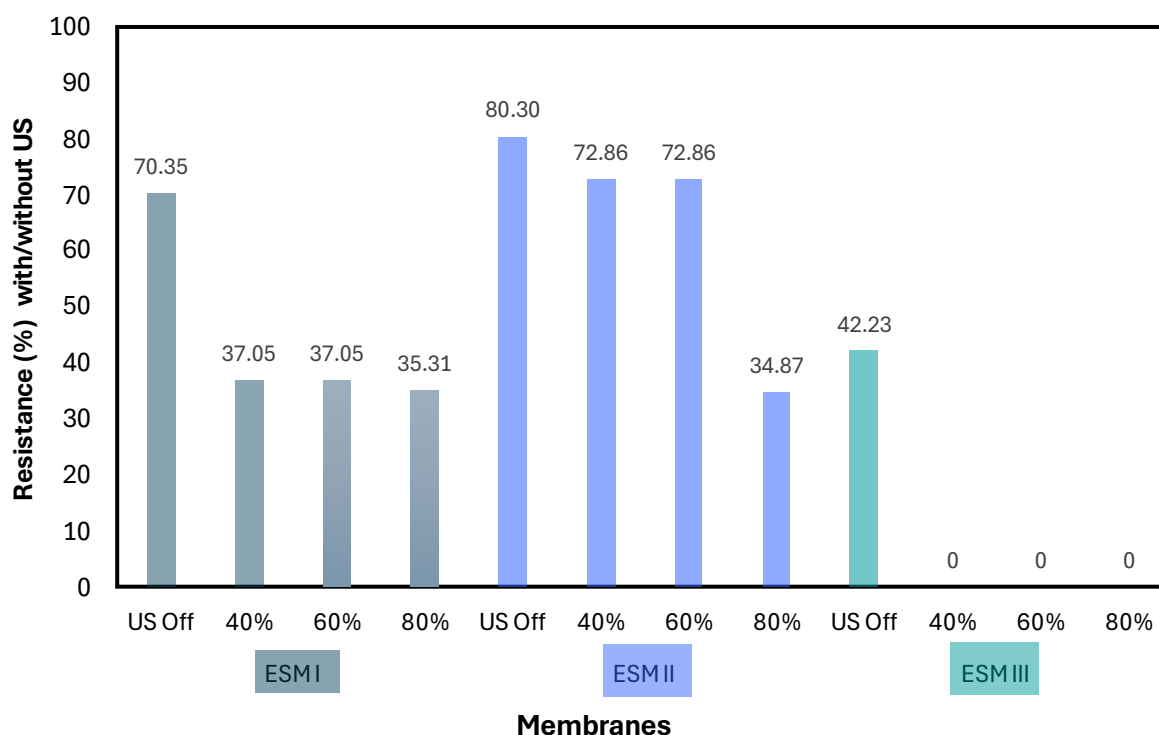


Figure 4.12 Fouling resistance (%) of ENM I, ENM II, and ENM III membranes during CNC filtration under different ultrasound amplitudes (0%, 40%, 60%, and 80%).

When no ultrasound was used, all membranes showed high fouling resistance: ENM II had the highest at 80.30%, followed by ENM I at 70.35%, and ENM III at 42.23%. This means that fouling naturally happened on all membranes under normal conditions. Once ultrasound was applied, the resistance values dropped in all membranes.

When ultrasound was not applied, all three membranes experienced high fouling resistance. ENM II had the highest value at 80.30%, followed by ENM I at 70.35%, and ENM III at 42.23%. After ultrasound was introduced, a notable reduction in resistance was observed. For ENM I, the resistance dropped to approximately 35–37%, showing that ultrasound helped to reduce surface fouling. ENM II showed limited improvement at lower amplitudes (40% and 60%) but decreased significantly to 34.87% at 80%, indicating that higher ultrasound intensity was more effective. ENM III, on the other hand, showed no resistance under all ultrasound

conditions, suggesting that fouling was completely prevented during filtration when ultrasound was applied.

4.5.4 US Enhancement Factor of ENMs During CNC Filtration

The US enhancement factor shows how much ultrasound improves membrane performance by comparing the flux with and without ultrasound. A higher factor means better improvement. Figure 4.13 shows UEF values for ENM I, ENM II, and ENM III at three ultrasound power levels: 1.0, 2.0, and 3.0 W/cm².

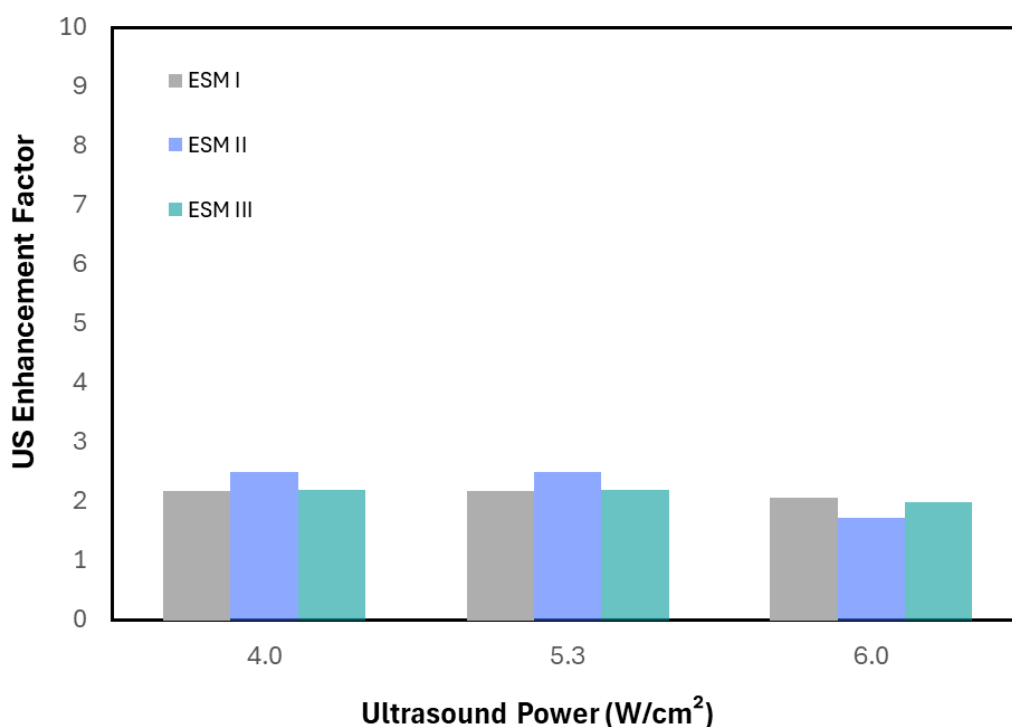


Figure 4.13 Ultrasound enhancement factor of ENM I, ENM II, and ENM III at different US levels (4.0, 5.3, and 6.0 W/cm²) during CNC filtration.

These results show that ultrasound has a modest but positive effect on the filtration performance of ESM membranes. The enhancement factors remained relatively low and consistent across all three membranes (ESM I–III), with only slight variation between different ultrasound power levels (4.0, 5.3, and 6.0 W/cm²). No clear trend of increasing enhancement with power was observed. The small differences in response may be attributed to minor variations in membrane structure or surface properties, but overall, the effect of ultrasound appears similar across all tested ESM configurations. SAXS measurements under these specific conditions could provide further insight into the structural organization of the fouling layer and help clarify why ultrasound enhancement remains limited in ESM membranes.

4.6 Structural Analysis of ENMs

This section presents the structural characterization of ENMs performed using SEM and SAXS. These techniques were employed to assess both the surface morphology and internal nanostructure of the membranes under different conditions.

4.6.1 SEM Characterization of ENMs

Several membrane samples were analyzed to evaluate their homogeneity, fiber structure, and mechanical response under different conditions, including exposure to ultrasound, cross-flow, and pressure.

A. Batch I – ENM Morphology and Ultrasound Stability (No Pressure)

The first batch of membranes was examined before and after exposure to ultrasound (40%, 60%, 80%) and cross-flow, without pressure. Due to their small size, the membranes were supported by a PES backing. Figure 4.14 shows SEM images of two ENM samples from Batch I before and after exposure to ultrasound and cross-flow.

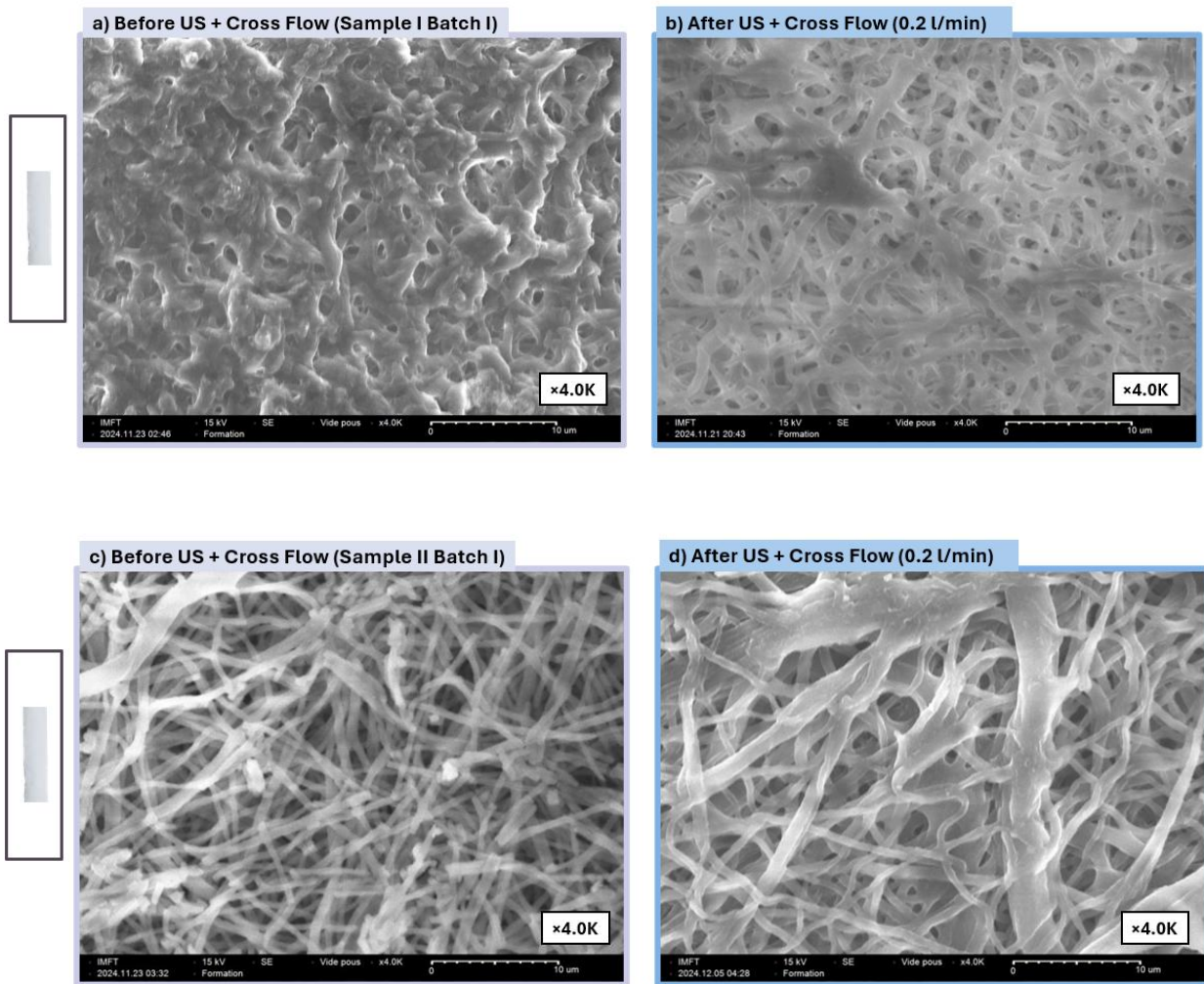


Figure 4.14 SEM images of ENMs from Batch I. (a) Sample I Before US and Cross Flow, (b) Sample I After US and Cross Flow, (c) Sample II Before US and Cross Flow, (d) Sample II After US and Cross Flow. All images taken at ×4.0K magnification.

SEM analysis of Batch I membranes before and after exposure to ultrasound and cross-flow (0.2 L/min) revealed that the ENMs surfaces were not homogeneous, with some areas appearing

dense and compact while others showed a more open fibrous structure. This variation was likely due to inconsistencies during electrospinning. After treatment with US and cross-flow, the denser regions became more porous, indicating that ultrasound might have loosen the packed fibers. In contrast, membranes that were already porous (Sample II) remained unchanged, suggesting good structural stability under the applied conditions. No visible damage, tearing, or fiber breakage was observed in any of the samples, confirming that the membranes could withstand US and flow without mechanical failure.

B. Batch II – ENM Morphology Analysis (No Pressure)

In this part of the study, ENMs from Batch II were tested under cross-flow and applied pressure to evaluate their mechanical stability and surface morphology. The membranes had dimensions of 4×1 cm and were tested using the newly available filtration cell optimized for this size without the use of PES as support. The tests were conducted at a flow rate of 0.2 L/min, pressure of 1.2 bar. Figure 4.15 shows SEM images that illustrate the structural changes in the membranes before and after exposure to pressure and crossflow.

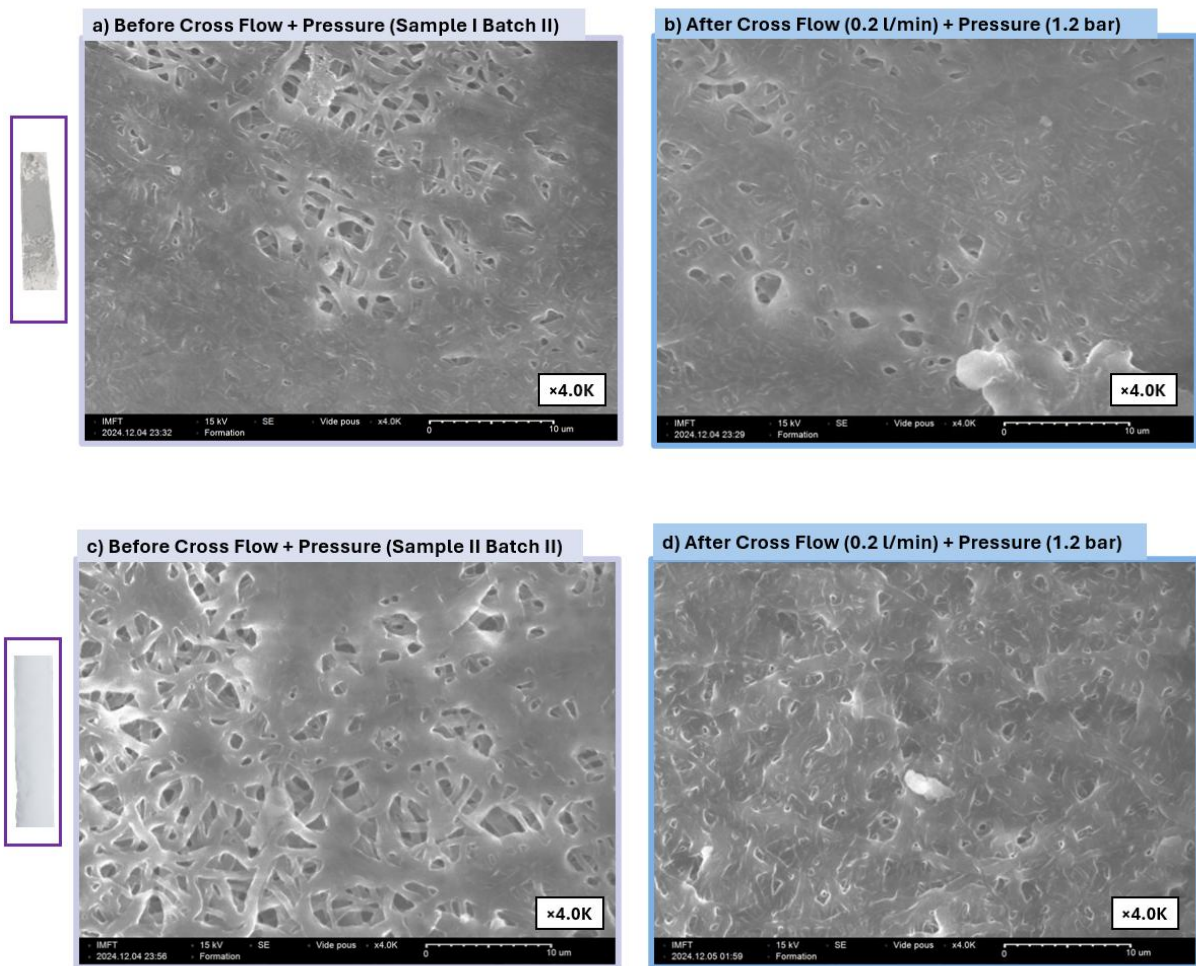


Figure 4.15 SEM images of Batch II ENMs before and after exposure to cross-flow (0.2 L/min) and pressure (1.2 bar). Images (a) and (c) show the membrane surface before testing, while (b) and (d) present the same membranes after treatment.

Batch II membranes were fabricated in a larger size (4×1 cm) and appeared either fully white or partially transparent. These samples were tested under cross-flow (0.2 L/min) and pressure (1.2 bar), but none produced measurable flux. As shown in Figure 4.13, SEM images revealed that both membrane types experienced visible compaction, with pore structures collapsing after pressure exposure. This structural compression explains the lack of flux and confirms that the membranes, although intact, were too fragile to maintain porosity under pressure. Therefore, it was concluded that lower operating pressures are more suitable for these membranes.

C. Batch II – Performance Stability of ENMs Used in CNC Filtration

Batch II also included smaller ENMs (2×1 cm), which were used for CNC filtration experiments. Since the filtration cell was not designed for this membrane size, the samples were placed on a PES support with cuts to ensure proper filtration. The membranes were tested under 0.5 bar pressure, 0.2 L/min cross-flow, and ultrasound at 40%, 60%, and 80% amplitude. Figure 4.16 presents SEM images taken before and after filtration.

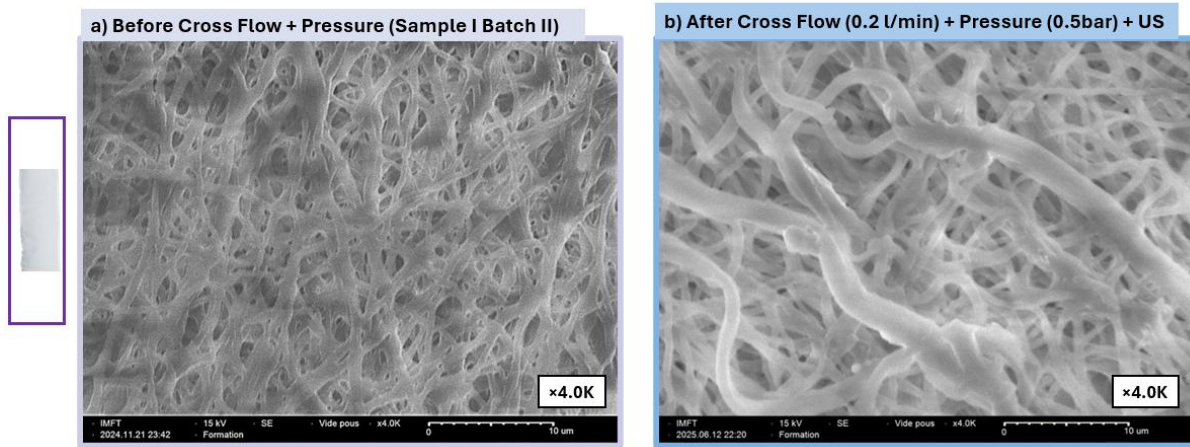


*Figure 4.16 SEM images of ENMs (Batch II) before and after CNC filtration using 0.5 bar pressure, 0.2 L/min cross-flow, and ultrasound at 40%, 60%, and 80% amplitude.
(a) Membrane surface before filtration; (b) membrane surface after filtration*

The SEM images in Figure 4.14 reveal that after exposure to 0.5 bar pressure, 0.2 L/min cross-flow, and ultrasound, the membrane maintained its structural integrity and even appeared slightly more porous. The fibers remained well-defined, with no signs of breakage or compaction. These results suggest that the membranes are stable under these operating conditions and can safely be used for CNC filtration without risk of structural damage.

4.6.1 SAXS Measurements for CNC filtration with ENMs

This section presents an analysis of CNC behavior during dead-end filtration, using SAXS to evaluate both the concentration profile and the SAXS patterns. The objective is to study the CNC accumulation within ENMs supported on PES membrane with cuts. Filtration was conducted at a constant pressure of 0.6 bar and a temperature of 20 °C for 15 hours.

Concentration Profiles

The nanoscale distribution of cellulose nanocrystals (CNCs) during dead-end filtration was evaluated using Small-Angle X-ray Scattering (SAXS). Measurements were conducted under constant operating conditions of 0.6 bar pressure and 20 °C, in dead-end mode to simulate high fouling risk environments without crossflow. SAXS data was collected at multiple depths (every 250 μm) from the membrane surface up to the bulk, capturing local CNC concentration profiles over a 15-hour filtration period. The CNC concentration is shown in Figure 4.17.

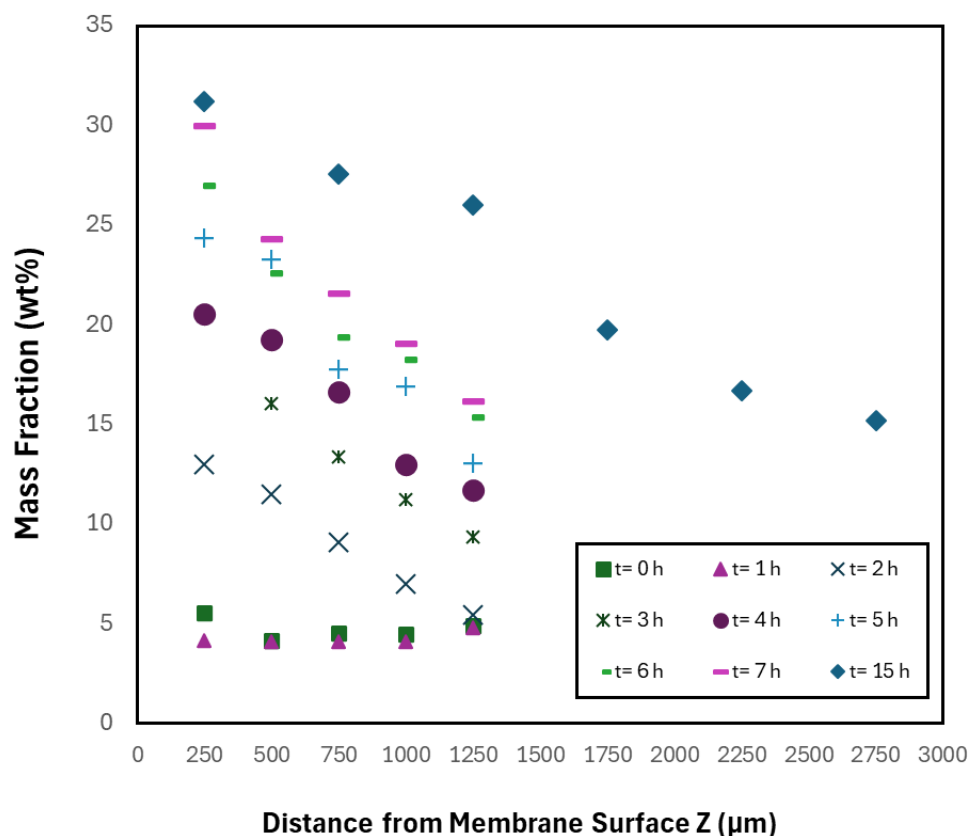


Figure 4.17 The CNC mass fraction (wt%) as a function of depth (Z) from the membrane surface, tracked over a 15-hour period.

SAXS measurements showed that CNC accumulation began almost immediately at the membrane surface (defined as 250 μm), with a rapid increase in concentration during the first 1–2 hours of filtration. A steep rise was observed near the surface (250–500 μm), indicating the onset of early fouling. Between hours 1 and 3, CNC concentration continued to increase and extended progressively deeper into the membrane structure, reaching depths of approximately 1250 μm . This trend reflects sustained particle retention and the formation of a growing fouling layer due to convective transport and the absence of shear in the dead-end set up.

Filtration ceased 7 hours as a result of complete membrane blockage. The rapid buildup of CNCs led to the formation of a dense fouling layer that significantly reduced flow through the PES + ENM system. Beyond this point, no further particle transport occurred, and changes in CNC concentration at later time points (e.g., 7 h and 15 h) are likely due to local diffusion or evaporation effects under static conditions.

4.6.2 SAXS Scattering Patterns

The 2D SAXS scattering patterns shown in Figure 4.18 provide insight into the structural evolution of CNC across the filtration cell over time and at varying distances from the membrane surface.

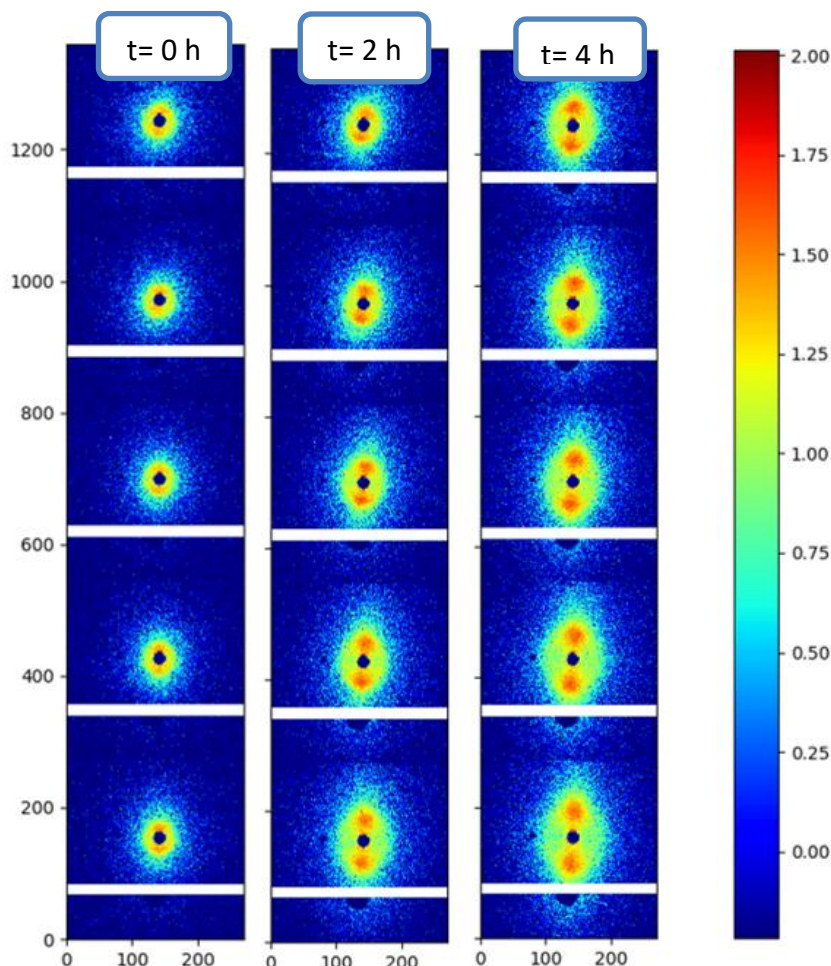


Figure 4.18 2D SAXS patterns at various depths for $t = 0$ h, 2 h, and 4 h.

The 2D SAXS patterns revealed the structural evolution of CNCs during the early stages of dead-end filtration. At $t = 0$ h, the scattering patterns at all depths appeared isotropic and low in intensity, indicating a uniformly dispersed CNC suspension with no significant aggregation or directional orientation. After 2 hours, the scattering patterns near the membrane surface became stronger, indicating that CNCs had started to accumulate. The patterns also began to stretch slightly, suggesting that the CNCs were beginning to align due to pressure. By 4 hours, this effect became more noticeable, showing that more CNCs had collected and were becoming more organized. Overall, the results show that CNCs mainly built up near the membrane surface and gradually became more aligned over time. This indicates that fouling development occurred primarily in the upper part of the membrane and became more structured as filtration continued.

The fouling development in ENM membranes appears to occur more rapidly than in PES membranes. This can be attributed to the higher permeate fluxes of ENMs, which lead to a greater

mass of CNCs being transported to the membrane surface over time. As a result, concentration polarization builds up more quickly, accelerating fouling. This faster accumulation may explain the limited impact of ultrasound in ENMs compared to PES membranes, as the dense fouling layer forms sooner and may be less responsive to acoustic disruption.

4.7 Comparison Between ENMs and PES Membranes

4.7.1 Membrane Permeability

The permeability behavior of PES and ENMs differed significantly under both baseline and ultrasound-assisted conditions. PES membranes exhibited stable and reproducible flux profiles, consistent with their well-characterized ultrafiltration performance. The permeability remained within expected ultrafiltration ranges, and the membranes showed minimal performance variation over time. In contrast, the ENMs demonstrated significantly higher permeability. However, this advantage was accompanied by higher variability between batches.

4.7.2 Membrane Stability

PES membranes retained their integrity throughout filtration, with no evidence of compaction or performance degradation under 20 kHz ultrasound exposure. Conversely, unsupported ENMs, particularly those of reduced thickness, were prone to mechanical instability. SEM imaging revealed pore expansion and fiber distortion under high pressure, which impaired permeability and increased resistance over time. This behavior was partially mitigated by introducing a supporting PES layer.

4.7.3 Ultrasound Response and Fouling Behavior

Fouling in PES membranes was largely reversible through ultrasound-assisted cleaning, attributed to the relatively simple surface deposition mechanisms. In contrast, ENMs exhibited more complex fouling dynamics. Their high porosity facilitated deeper CNC penetration and internal fouling, which ultrasound was often unable to fully remove during US-off cycles. The fouling resistance in ENMs varied widely with batch quality, membrane fabrication, and support structure. Notably, the presence of internal fouling in ENMs made sustained fouling control more challenging than in PES membranes.

4.7.4 Limitations

Despite the promising outcomes of this study, several limitations should be acknowledged. The variability in ENM batch fabrication introduced uncertainties in reproducibility and structural consistency, which directly affected the filtration outcomes. Membrane thickness, fiber alignment, and porosity were not uniformly controlled across all samples, making comparative analysis more complex. The filtration cell required a reduction in the flow channel length from 10 cm to 4 cm to accommodate smaller membrane samples. While this modification enabled sealing and stable operation, it compromised the optimization of ultrasound transmission. The acoustic field was originally designed for a longer path length and was not fully adapted for the new geometry, potentially leading to non-uniform ultrasonic energy distribution across the membrane surface and reduced effectiveness in fouling mitigation.

The attempts to characterize pore size distribution using mercury intrusion porosimetry were ultimately unsuccessful. The ENM samples lacked the minimum mass required by the instrument. Moreover, delays in membrane fabrication and limited availability of ENM samples in the optimized size made it difficult to carry out repeated tests and fully optimize the operating conditions. As a result, some planned experiments could not be completed.

5 Conclusion & Future Studies

This study explored the filtration performance, fouling behavior, and structural response of ENMs, compared to PES membranes under ultrasound-assisted conditions. The use of ultrasound significantly improved permeability in both membrane types, with a more pronounced effect in ENMs exhibiting high fiber uniformity and mechanical stability. SAXS analysis provided structural insights in situ, revealing how CNCs accumulate and distribute within the membrane module over time.

While PES membranes demonstrated stable flux and fouling resistance across all conditions, ENMs showed more variable performance. Their high intrinsic porosity allowed greater initial permeability, but also led to internal fouling and mechanical instability, especially in unsupported or thinner configurations. Ultrasound was effective in partially mitigating these effects but did not fully prevent fouling during US-off phases. Structural reinforcement using a PES support layer improved ENM stability and performance.

The SAXS measurements provided valuable insights into the nanoscale structural evolution of CNC suspensions during membrane filtration. By analyzing interparticle distances and concentration gradients across the membrane module over time, SAXS revealed the gradual buildup of CNCs near the membrane surface, formation of concentration polarization and fouling layer. Although ultrasound was not applied during the SAXS experiments, the data served as a structural reference for understanding how fouling progresses. These results, when interpreted alongside the dynamic filtration data, suggest that ultrasound likely plays a key role in reducing such structural accumulation. This data will help illustrate the region's most susceptible to fouling and emphasize the importance of localized fouling control.

Future research should prioritize enhancing the mechanical stability and structural consistency of electrospun nanofibrous membranes. This can be achieved by optimizing polymer selection, refining fiber alignment, and adjusting key electrospinning parameters to produce more uniform membranes. A systematic investigation into how specific fiber morphologies respond to ultrasound during filtration would provide valuable insights for fabricating ENMs to dynamic filtration conditions. Producing membranes in larger, standardized formats will improve batch-to-batch consistency and allow for more experimental comparisons.

Additional structural characterization methods, such as mercury intrusion porosimetry and dynamic vapor sorption (DVS), should be employed to quantify membrane porosity, pore connectivity, and sorption behavior more comprehensively with or without US. These data are critical for linking membrane structure to fouling dynamics and for guiding future design improvements.

Expanding SAXS analysis to include crossflow filtration configurations and ultrasound exposure will also be an important step forward. Performing in situ SAXS on larger membrane areas under continuous operation would yield more realistic information on CNC accumulation, fouling layer development and distribution of concentration polarization.

References

- Aghapour Aktij, S., Taghipour, A., Rahimpour, A., Mollahosseini, A. and Tiraferri, A. (2020) 'A critical review on ultrasonic-assisted fouling control and cleaning of fouled membranes', *Ultrasonics*, 108, p. 106228. Available at: <https://doi.org/10.1016/j.ultras.2020.106228>.
- Alventosa-deLara, E., Barredo-Damas, S., Alcaina-Miranda, M.I. and Iborra-Clar, M.I. (2014) 'Study and optimization of the ultrasound-enhanced cleaning of an ultrafiltration ceramic membrane through a combined experimental–statistical approach', *Ultrasonics Sonochemistry*, 21(3), pp. 1222–1234. Available at: <https://doi.org/10.1016/j.ultsonch.2013.10.022>.
- Asif Khan, R.M., Ahmad, N.M., Nasir, H., Mahmood, A., Iqbal, M. and Janjua, H.A. (2023) 'Antifouling and Water Flux Enhancement in Polyethersulfone Ultrafiltration Membranes by Incorporating Water-Soluble Cationic Polymer of Poly [2-(Dimethyl amino) ethyl Methacrylate]', *Polymers*, 15(13), p. 2868. Available at: <https://doi.org/10.3390/polym15132868>.
- Awad, E.Sh., Sabirova, T.M., Tretyakova, N.A., Alsahy, Q.F., Figoli, A. and Salih, I.K. (2021a) 'A Mini-Review of Enhancing Ultrafiltration Membranes (UF) for Wastewater Treatment: Performance and Stability', *ChemEngineering*, 5(3), p. 34. Available at: <https://doi.org/10.3390/chemengineering5030034>.
- Awad, E.Sh., Sabirova, T.M., Tretyakova, N.A., Alsahy, Q.F., Figoli, A. and Salih, I.K. (2021b) 'A Mini-Review of Enhancing Ultrafiltration Membranes (UF) for Wastewater Treatment: Performance and Stability', *ChemEngineering*, 5(3), p. 34. Available at: <https://doi.org/10.3390/chemengineering5030034>.
- Azami, S. and Amirinejad, M. (2019) 'Effect of Ultrasonication on Membrane Structure and Flux Recovery for Whey Ultrafiltration', *Journal of Membrane Science and Research* [Pre-print], (Online First). Available at: <https://doi.org/10.22079/jmsr.2019.96835.1225>.
- Band, M., Gutman, M., Faerman, V., Korngold, E., Kost, J., Plath, P.J. and Gontar, V. (1997) 'Influence of specially modulated ultrasound on the water desalination process with ion-exchange hollow fibers', *Desalination*, 109(3), pp. 303–313. Available at: [https://doi.org/10.1016/S0011-9164\(97\)00076-3](https://doi.org/10.1016/S0011-9164(97)00076-3).
- Bhangu, S.K. and Ashokkumar, M. (2016) 'Theory of Sonochemistry', *Topics in Current Chemistry*, 374(4). Available at: <https://doi.org/10.1007/s41061-016-0054-y>.
- Bolton, G.R., Boesch, A.W. and Lazzara, M.J. (2006) 'The effects of flow rate on membrane capacity: Development and application of adsorptive membrane fouling models', *Journal of Membrane Science*, 279(1–2), pp. 625–634. Available at: <https://doi.org/10.1016/j.memsci.2005.12.057>.
- Borea, L., Naddeo, V., Shalaby, M.S., Zarra, T., Belgiorno, V., Abdalla, H. and Shaban, A.M. (2018) 'Wastewater treatment by membrane ultrafiltration enhanced with ultrasound: Effect of membrane flux and ultrasonic frequency', *Ultrasonics*, 83, pp. 42–47. Available at: <https://doi.org/10.1016/j.ultras.2017.06.013>.

- Cai, M., Wang, S. and Liang, H. (2012) 'Optimization of ultrasound-assisted ultrafiltration of Radix astragalus extracts with hollow fiber membrane using response surface methodology', *Separation and Purification Technology*, 100, pp. 74–81. Available at: <https://doi.org/10.1016/j.seppur.2012.09.002>.
- Cai, M., Wang, S., Zheng, Y. and Liang, H. (2009) 'Effects of ultrasound on ultrafiltration of Radix astragalus extract and cleaning of fouled membrane', *Separation and Purification Technology*, 68(3), pp. 351–356. Available at: <https://doi.org/10.1016/j.seppur.2009.06.013>.
- Cai, M., Zhao, S. and Liang, H. (2010) 'Mechanisms for the enhancement of ultrafiltration and membrane cleaning by different ultrasonic frequencies', *Desalination*, 263(1–3), pp. 133–138. Available at: <https://doi.org/10.1016/j.desal.2010.06.049>.
- Camara, H.W.D., Doan, H. and Lohi, A. (2020) 'In-situ ultrasound-assisted control of polymeric membrane fouling', *Ultrasonics*, 108, p. 106206. Available at: <https://doi.org/10.1016/j.ultras.2020.106206>.
- Chai, X., Kobayashi, T. and Fujii, N. (1998) 'Ultrasound effect on cross-flow filtration of polyacrylonitrile ultrafiltration membranes', *Journal of Membrane Science*, 148(1), pp. 129–135. Available at: [https://doi.org/10.1016/S0376-7388\(98\)00145-8](https://doi.org/10.1016/S0376-7388(98)00145-8).
- Chai, X., Kobayashi, T. and Fujii, N. (1999) 'Ultrasound-associated cleaning of polymeric membranes for water treatment', *Separation and Purification Technology*, 15(2), pp. 139–146. Available at: [https://doi.org/10.1016/s1383-5866\(98\)00091-4](https://doi.org/10.1016/s1383-5866(98)00091-4).
- Chen, D., Weavers, L.K. and Walker, H.W. (2006a) 'Ultrasonic control of ceramic membrane fouling by particles: Effect of ultrasonic factors', *Ultrasonics Sonochemistry*, 13(5), pp. 379–387. Available at: <https://doi.org/10.1016/j.ultsonch.2005.07.004>.
- Chen, D., Weavers, L.K. and Walker, H.W. (2006b) 'Ultrasonic control of ceramic membrane fouling by particles: Effect of ultrasonic factors', *Ultrasonics Sonochemistry*, 13(5), pp. 379–387. Available at: <https://doi.org/10.1016/j.ultsonch.2005.07.004>.
- Chen, H., Huang, M., Liu, Y., Meng, L. and Ma, M. (2020) 'Functionalized electrospun nano-fiber membranes for water treatment: A review', *Science of The Total Environment*, 739, p. 139944. Available at: <https://doi.org/10.1016/j.scitotenv.2020.139944>.
- Chen, Z., Xiao, T., Hu, D., Xu, J., Li, X., Jia, F., Wang, H., Gu, F., Su, H. and Zhang, Y. (2018) 'The performance and membrane fouling rate of a pilot-scale anaerobic membrane bioreactor for treating antibiotic solvent wastewater under different cross flow velocity', *Water Research*, 135, pp. 288–301. Available at: <https://doi.org/10.1016/j.watres.2018.02.027>.
- Collis, J., Manasseh, R., Liovic, P., Tho, P., Ooi, A., Petkovic-Duran, K. and Zhu, Y. (2010) 'Cavitation microstreaming and stress fields created by microbubbles', *Ultrasonics*, 50(2), pp. 273–279. Available at: <https://doi.org/10.1016/j.ultras.2009.10.002>.
- Desiriani, R., Susanto, H., Istirokhatun, T., Lin, Y., Aryanti, N., Abriyanto, H., Saputra, H. and Matsuyama, H. (2024) 'Preparation of polyethersulfone ultrafiltration membrane coated natural additives toward antifouling and antimicrobial agents for surface water filtration', *Journal of*

Environmental Chemical Engineering, 12(1), p. 111797. Available at: <https://doi.org/10.1016/j.jece.2023.111797>.

Di Bella, G. and Di Trapani, D. (2019) 'A Brief Review on the Resistance-in-Series Model in Membrane Bioreactors (MBRs)', *Membranes*, 9(2), p. 24. Available at: <https://doi.org/10.3390/membranes9020024>.

Dobosz, K.M., Kuo-Leblanc, C.A., Martin, T.J. and Schiffman, J.D. (2017) 'Ultrafiltration Membranes Enhanced with Electrospun Nanofibers Exhibit Improved Flux and Fouling Resistance', *Industrial & Engineering Chemistry Research*, 56(19), pp. 5724–5733. Available at: <https://doi.org/10.1021/acs.iecr.7b00631>.

Ehsani, M., Doan, H. and Lohi, A. (2021a) 'A comprehensive review of membrane fouling and cleaning methods with emphasis on ultrasound-assisted fouling control processes', *Korean Journal of Chemical Engineering*, 38(8), pp. 1531–1555. Available at: <https://doi.org/10.1007/s11814-021-0832-2>.

Ehsani, M., Doan, H. and Lohi, A. (2021b) 'A comprehensive review of membrane fouling and cleaning methods with emphasis on ultrasound-assisted fouling control processes', *Korean Journal of Chemical Engineering*, 38(8), pp. 1531–1555. Available at: <https://doi.org/10.1007/s11814-021-0832-2>.

Fan, L., Xu, Y., Zhou, X., Chen, F. and Fu, Q. (2018) 'Effect of salt concentration in spinning solution on fiber diameter and mechanical property of electrospun styrene-butadiene-styrene tri-block copolymer membrane', *Polymer*, 153, pp. 61–69. Available at: <https://doi.org/10.1016/j.polymer.2018.08.008>.

Fang, Z., Qi, X. and Smith, J. (eds) (2015) *Production of Biofuels and Chemicals with Ultrasound*. 1st ed. 2015. Dordrecht: Springer Netherlands : Imprint: Springer (Biofuels and Biorefineries, 4). Available at: <https://doi.org/10.1007/978-94-017-9624-8>.

Fetyan, N.A.H. and Salem Attia, T.M. (2020) 'Water purification using ultrasound waves: application and challenges', *Arab Journal of Basic and Applied Sciences*, 27(1), pp. 194–207. Available at: <https://doi.org/10.1080/25765299.2020.1762294>.

Field, R.W. and Pearce, G.K. (2011) 'Critical, sustainable and threshold fluxes for membrane filtration with water industry applications', *Advances in Colloid and Interface Science*, 164(1–2), pp. 38–44. Available at: <https://doi.org/10.1016/j.cis.2010.12.008>.

Gao, Y., Chen, D., Weavers, L.K. and Walker, H.W. (2012) 'Ultrasonic control of UF membrane fouling by natural waters: Effects of calcium, pH, and fractionated natural organic matter', *Journal of Membrane Science*, 401–402, pp. 232–240. Available at: <https://doi.org/10.1016/j.memsci.2012.02.009>.

He, Z., Miller, D.J., Kasemset, S., Paul, D.R. and Freeman, B.D. (2017) 'The effect of permeate flux on membrane fouling during microfiltration of oily water', *Journal of Membrane Science*, 525, pp. 25–34. Available at: <https://doi.org/10.1016/j.memsci.2016.10.002>.

- Heikkinen, J., Kyllönen, H., Järvelä, E., Grönroos, A. and Tang, C.Y. (2017) 'Ultrasound-assisted forward osmosis for mitigating internal concentration polarization', *Journal of Membrane Science*, 528, pp. 147–154. Available at: <https://doi.org/10.1016/j.memsci.2017.01.035>.
- Hengl, N., Jin, Y., Pignon, F., Baup, S., Mollard, R., Gondrexon, N., Magnin, A., Michot, L. and Paineau, E. (2014a) 'A new way to apply ultrasound in cross-flow ultrafiltration: Application to colloidal suspensions', *Ultrasonics Sonochemistry*, 21(3), pp. 1018–1025. Available at: <https://doi.org/10.1016/j.ultsonch.2013.11.008>.
- Hengl, N., Jin, Y., Pignon, F., Baup, S., Mollard, R., Gondrexon, N., Magnin, A., Michot, L. and Paineau, E. (2014b) 'A new way to apply ultrasound in cross-flow ultrafiltration: Application to colloidal suspensions', *Ultrasonics Sonochemistry*, 21(3), pp. 1018–1025. Available at: <https://doi.org/10.1016/j.ultsonch.2013.11.008>.
- Hilal, N., Ogunbiyi, O.O., Miles, N.J. and Nigmatullin, R. (2005) 'Methods Employed for Control of Fouling in MF and UF Membranes: A Comprehensive Review', *Separation Science and Technology*, 40(10), pp. 1957–2005. Available at: <https://doi.org/10.1081/ss-200068409>.
- HMTShirazi, R., Mohammadi, T., Asadi, A.A. and Tofighy, M.A. (2022) 'Electrospun nanofiber affinity membranes for water treatment applications: A review', *Journal of Water Process Engineering*, 47, p. 102795. Available at: <https://doi.org/10.1016/j.jwpe.2022.102795>.
- Idris, A., Mat Zain, N. and Noordin, M.Y. (2007) 'Synthesis, characterization and performance of asymmetric polyethersulfone (PES) ultrafiltration membranes with polyethylene glycol of different molecular weights as additives', *Desalination*, 207(1–3), pp. 324–339. Available at: <https://doi.org/10.1016/j.desal.2006.08.008>.
- Jain, A., Sengupta, S. and De, S. (2018) 'Fundamental Understanding of Fouling Mechanisms During Microfiltration of Bitter Gourd (*Momordica charantia*) Extract and Their Dependence on Operating Conditions', *Food and Bioprocess Technology*, 11(5), pp. 1012–1026. Available at: <https://doi.org/10.1007/s11947-018-2074-9>.
- Juang, R.-S., Chen, H.-L. and Chen, Y.-S. (2008) 'Membrane fouling and resistance analysis in dead-end ultrafiltration of *Bacillus subtilis* fermentation broths', *Separation and Purification Technology*, 63(3), pp. 531–538. Available at: <https://doi.org/10.1016/j.seppur.2008.06.011>.
- Kallioinen, M. and Mänttari, M. (2011) 'Influence of Ultrasonic Treatment on Various Membrane Materials: A Review', *Separation Science and Technology*, 46(9), pp. 1388–1395. Available at: <https://doi.org/10.1080/01496395.2011.571649>.
- Kobayashi, T., Chai, X. and Fujii, N. (1999) 'Ultrasound enhanced cross-flow membrane filtration', *Separation and Purification Technology*, 17(1), pp. 31–40. Available at: [https://doi.org/10.1016/S1383-5866\(99\)00023-4](https://doi.org/10.1016/S1383-5866(99)00023-4).
- Kobayashi, Takaomi, Kobayashi, Tsuyoshi, Hosaka, Y. and Fujii, N. (2003) 'Ultrasound-enhanced membrane-cleaning processes applied water treatments: influence of sonic frequency on filtration treatments', *Ultrasonics*, 41(3), pp. 185–190. Available at: [https://doi.org/10.1016/S0041-624X\(02\)00462-6](https://doi.org/10.1016/S0041-624X(02)00462-6).

- Koo, C.H., Mohammad, A.W., Suja', F. and Meor Talib, M.Z. (2012) 'Review of the effect of selected physicochemical factors on membrane fouling propensity based on fouling indices', *Desalination*, 287, pp. 167–177. Available at: <https://doi.org/10.1016/j.desal.2011.11.003>.
- Korolev, A.V., Korolev, A.A., Bolkunov, V.V. and Vasin, A.N. (2011) 'Ultrasonic cleaning of bearing components', *Russian Engineering Research*, 31(1), pp. 85–87. Available at: <https://doi.org/10.3103/S1068798X11010114>.
- Kyllönen, H., Pirkonen, P., Nyström, M., Nuortila-Jokinen, J. and Grönroos, A. (2006) 'Experimental aspects of ultrasonically enhanced cross-flow membrane filtration of industrial wastewater', *Ultrasonics Sonochemistry*, 13(4), pp. 295–302. Available at: <https://doi.org/10.1016/j.ultsonch.2005.04.006>.
- Kyllönen, H.M., Pirkonen, P. and Nyström, M. (2005) 'Membrane filtration enhanced by ultrasound: a review', *Desalination*, 181(1–3), pp. 319–335. Available at: <https://doi.org/10.1016/j.desal.2005.06.003>.
- Lamminen, M. (2004) 'Mechanisms and factors influencing the ultrasonic cleaning of particle-fouled ceramic membranes', *Journal of Membrane Science*, 237(1–2), pp. 213–223. Available at: <https://doi.org/10.1016/j.memsci.2004.02.031>.
- Latt, K.K. and Kobayashi, T. (2006) 'Ultrasound-membrane hybrid processes for enhancement of filtration properties', *Ultrasonics Sonochemistry*, 13(4), pp. 321–328. Available at: <https://doi.org/10.1016/j.ultsonch.2005.05.002>.
- Leighton, T.G. (1994) *The acoustic bubble*. London San Diego New York [etc.]: Academic press.
- Leighton, T.G. (2007) 'What is ultrasound?', *Progress in Biophysics and Molecular Biology*, 93(1–3), pp. 3–83. Available at: <https://doi.org/10.1016/j.pbiomolbio.2006.07.026>.
- Lenart, I. and Ausländer, D. (1980) 'The effect of ultrasound on diffusion through membranes', *Ultrasonics*, 18(5), pp. 216–218. Available at: [https://doi.org/10.1016/0041-624X\(80\)90123-7](https://doi.org/10.1016/0041-624X(80)90123-7).
- Li, J. (2002) 'Ultrasonic cleaning of nylon microfiltration membranes fouled by Kraft paper mill effluent', *Journal of Membrane Science*, 205(1–2), pp. 247–257. Available at: [https://doi.org/10.1016/s0376-7388\(02\)00121-7](https://doi.org/10.1016/s0376-7388(02)00121-7).
- Li, X., Wang, Q., Guo, S., He, C., Mao, H., Meng, X., Zhou, Z. and Zheng, T. (2025) 'Ultrasonic assisted in-situ synthesis of photocatalytic ZnO on PVDF membrane surface for fouling degradation', *Journal of Membrane Science*, 715, p. 123450. Available at: <https://doi.org/10.1016/j.memsci.2024.123450>.
- Li, X., Yu, J. and Nnanna, A.G.A. (2011) 'Fouling mitigation for hollow-fiber UF membrane by sonication', *Desalination*, 281, pp. 23–29. Available at: <https://doi.org/10.1016/j.desal.2011.07.036>.
- Luján-Facundo, M.J., Mendoza-Roca, J.A., Cuartas-Urbe, B. and Álvarez-Blanco, S. (2016) 'Study of membrane cleaning with and without ultrasounds application after fouling with three model dairy solutions', *Food and Bioproducts Processing*, 100, pp. 36–46. Available at: <https://doi.org/10.1016/j.fbp.2016.06.011>.

Mandin, S., Metilli, L., Karrouch, M., Blèsès, D., Lancelon-Pin, C., Sailer, P., Chèvremont, W., Paineau, E., Putaux, J.-L., Hengl, N., Jean, B. and Pignon, F. (2024) ‘Multiscale study of the chiral self-assembly of cellulose nanocrystals during the frontal ultrafiltration process’, *Nanoscale*, 16(40), pp. 19100–19115. Available at: <https://doi.org/10.1039/D4NR02840F>.

Maurya, A.K., Mias, E., Schoeller, J., Collings, I.E., Rossi, R.M., Dommann, A. and Neels, A. (2022) ‘Understanding multiscale structure–property correlations in PVDF-HFP electrospun fiber membranes by SAXS and WAXS’, *Nanoscale Advances*, 4(2), pp. 491–501. Available at: <https://doi.org/10.1039/D1NA00503K>.

Mirzaie, A. and Mohammadi, T. (2012) ‘Effect of ultrasonic waves on flux enhancement in microfiltration of milk’, *Journal of Food Engineering*, 108(1), pp. 77–86. Available at: <https://doi.org/10.1016/j.jfoodeng.2011.07.026>.

Mulyati, S., Muchtar, S., Razi, F., Ambarita, A.C., Luthfiana, A., Aulia, M.P. and Bilad, M.R. (2025) ‘Enhancing polyethersulfone membrane durability and stability through Eco-friendly green silica from natural kaolin for water treatment applications’, *Results in Engineering*, 26, p. 105340. Available at: <https://doi.org/10.1016/j.rineng.2025.105340>.

Muthukumaran, S., Kentish, S., Ashokkumar, M. and Stevens, G. (2005) ‘Mechanisms for the ultrasonic enhancement of dairy whey ultrafiltration’, *Journal of Membrane Science*, 258(1–2), pp. 106–114. Available at: <https://doi.org/10.1016/j.memsci.2005.03.001>.

Muthukumaran, Shobha, Kentish, S., Lalchandani, S., Ashokkumar, M., Mawson, R., Stevens, G.W. and Grieser, F. (2005) ‘The optimisation of ultrasonic cleaning procedures for dairy fouled ultrafiltration membranes’, *Ultrasonics Sonochemistry*, 12(1–2), pp. 29–35. Available at: <https://doi.org/10.1016/j.ultsonch.2004.05.007>.

Muthukumaran, S., Kentish, S.E., Stevens, G.W., Ashokkumar, M. and Mawson, R. (2007) ‘The application of ultrasound to dairy ultrafiltration: The influence of operating conditions’, *Journal of Food Engineering*, 81(2), pp. 364–373. Available at: <https://doi.org/10.1016/j.jfoodeng.2006.11.008>.

Muthukumaran, S., Yang, K., Seuren, A., Kentish, S., Ashokkumar, M., Stevens, G.W. and Grieser, F. (2004) ‘The use of ultrasonic cleaning for ultrafiltration membranes in the dairy industry’, *Separation and Purification Technology*, 39(1–2), pp. 99–107. Available at: <https://doi.org/10.1016/j.seppur.2003.12.013>.

Naddeo, V., Borea, L. and Belgiorno, V. (2015) ‘Sonochemical control of fouling formation in membrane ultrafiltration of wastewater: Effect of ultrasonic frequency’, *Journal of Water Process Engineering*, 8, pp. e92–e97. Available at: <https://doi.org/10.1016/j.jwpe.2014.12.005>.

Naji, O., Al-juboori, R.A., Khan, A., Yadav, S., Altaee, A., Alpatova, A., Soukane, S. and Ghaffour, N. (2021) ‘Ultrasound-assisted membrane technologies for fouling control and performance improvement: A review’, *Journal of Water Process Engineering*, 43, p. 102268. Available at: <https://doi.org/10.1016/j.jwpe.2021.102268>.

Nghiem, L.D. and Hawkes, S. (2007) ‘Effects of membrane fouling on the nanofiltration of pharmaceutically active compounds (PhACs): Mechanisms and role of membrane pore size’,

Separation and Purification Technology, 57(1), pp. 176–184. Available at: <https://doi.org/10.1016/j.seppur.2007.04.002>.

Peinemann, K. and Pereira Nunes, S. (eds) (2010) *Membrane Technology: Volume 4: Membranes for Water Treatment*. 1st edn. Wiley. Available at: <https://doi.org/10.1002/9783527631407>.

Popović, S., Djurić, M., Milanović, S., Tekić, M.N. and Lukić, N. (2010) ‘Application of an ultrasound field in chemical cleaning of ceramic tubular membrane fouled with whey proteins’, *Journal of Food Engineering*, 101(3), pp. 296–302. Available at: <https://doi.org/10.1016/j.jfoodeng.2010.07.012>.

Qasim, M., Darwish, N.N., Mhiyo, S., Darwish, N.A. and Hilal, N. (2018) ‘The use of ultrasound to mitigate membrane fouling in desalination and water treatment’, *Desalination*, 443, pp. 143–164. Available at: <https://doi.org/10.1016/j.desal.2018.04.007>.

Qu, F., Liang, H., Zhou, J., Nan, J., Shao, S., Zhang, J. and Li, G. (2014) ‘Ultrafiltration membrane fouling caused by extracellular organic matter (EOM) from *Microcystis aeruginosa*: Effects of membrane pore size and surface hydrophobicity’, *Journal of Membrane Science*, 449, pp. 58–66. Available at: <https://doi.org/10.1016/j.memsci.2013.07.070>.

Rattana-arporn, P. and Poompradub, S. (2024) ‘Polyethersulfone/silica composite membrane for desalination’, *Separation and Purification Technology*, 345, p. 127395. Available at: <https://doi.org/10.1016/j.seppur.2024.127395>.

Secondes, M.F.N., Naddeo, V., Belgiorno, V. and Ballesteros, F. (2014) ‘Removal of emerging contaminants by simultaneous application of membrane ultrafiltration, activated carbon adsorption, and ultrasound irradiation’, *Journal of Hazardous Materials*, 264, pp. 342–349. Available at: <https://doi.org/10.1016/j.jhazmat.2013.11.039>.

Simon, A., Gondrexon, N., Taha, S., Cabon, J. and Dorange, G. (2000) ‘Low-Frequency Ultrasound to Improve Dead-End Ultrafiltration Performance’, *Separation Science and Technology*, 35(16), pp. 2619–2637. Available at: <https://doi.org/10.1081/SS-100102359>.

Tanudjaja, H.J., Anantharaman, A., Ng, A.Q.Q., Ma, Y., Tanis-Kanbur, M.B., Zydney, A.L. and Chew, J.W. (2022) ‘A review of membrane fouling by proteins in ultrafiltration and microfiltration’, *Journal of Water Process Engineering*, 50, p. 103294. Available at: <https://doi.org/10.1016/j.jwpe.2022.103294>.

Thombre, N.V., Gadhekar, A.P., Patwardhan, A.V. and Gogate, P.R. (2020) ‘Ultrasound induced cleaning of polymeric nanofiltration membranes’, *Ultrasonics Sonochemistry*, 62, p. 104891. Available at: <https://doi.org/10.1016/j.ultsonch.2019.104891>.

Verraes, T., Lepoint-Mullie, F., Lepoint, T. and Longuet-Higgins, M.S. (2000) ‘Experimental study of the liquid flow near a single sonoluminescent bubble’, *The Journal of the Acoustical Society of America*, 108(1), pp. 117–125. Available at: <https://doi.org/10.1121/1.429449>.

Wang, A., Xu, H., Chen, C., Chen, L., Lin, T., Ma, J. and Ding, M. (2024) ‘Critical review on advances and perspectives of ultrasound assisted membrane technologies for water

purification', *Chemical Engineering Journal*, 482, p. 148873. Available at: <https://doi.org/10.1016/j.cej.2024.148873>.

Wang, J., Gao, X., Xu, Y., Wang, Q., Zhang, Y., Wang, X. and Gao, C. (2016) 'Ultrasonic-assisted acid cleaning of nanofiltration membranes fouled by inorganic scales in arsenic-rich brackish water', *Desalination*, 377, pp. 172–177. Available at: <https://doi.org/10.1016/j.desal.2015.09.021>.

Wang, Z., Ma, J., Tang, C.Y., Kimura, K., Wang, Q. and Han, X. (2014) 'Membrane cleaning in membrane bioreactors: A review', *Journal of Membrane Science*, 468, pp. 276–307. Available at: <https://doi.org/10.1016/j.memsci.2014.05.060>.

Wolloch, L. and Kost, J. (2010) 'The importance of microjet vs shock wave formation in sonophoresis', *Journal of Controlled Release*, 148(2), pp. 204–211. Available at: <https://doi.org/10.1016/j.jconrel.2010.07.106>.

Xu, H., Xiao, K., Yu, J., Huang, B., Wang, X., Liang, S., Wei, C., Wen, X. and Huang, X. (2020) 'A Simple Method to Identify the Dominant Fouling Mechanisms during Membrane Filtration Based on Piecewise Multiple Linear Regression', *Membranes*, 10(8), p. 171. Available at: <https://doi.org/10.3390/membranes10080171>.

Yao Jin (2014) *Cross-flow ultrafiltration of colloids : characterization of the mechanisms at nanometer length scales and enhanced by ultrasound*. Thesis. Université de Grenoble. Available at: https://theses.hal.science/tel-01249558v1/file/JIN_2014_archivage.pdf.

Yao, Y., Pan, Y. and Liu, S. (2020) 'Power ultrasound and its applications: A state-of-the-art review', *Ultrasonics Sonochemistry*, 62, p. 104722. Available at: <https://doi.org/10.1016/j.ultsonch.2019.104722>.

Yusof, N.S.M., Babgi, B., Alghamdi, Y., Aksu, M., Madhavan, J. and Ashokkumar, M. (2016a) 'Physical and chemical effects of acoustic cavitation in selected ultrasonic cleaning applications', *Ultrasonics Sonochemistry*, 29, pp. 568–576. Available at: <https://doi.org/10.1016/j.ultsonch.2015.06.013>.

Yusof, N.S.M., Babgi, B., Alghamdi, Y., Aksu, M., Madhavan, J. and Ashokkumar, M. (2016b) 'Physical and chemical effects of acoustic cavitation in selected ultrasonic cleaning applications', *Ultrasonics Sonochemistry*, 29, pp. 568–576. Available at: <https://doi.org/10.1016/j.ultsonch.2015.06.013>.

Zhang, R., Huang, Y., Sun, C., Xiaozhen, L., Bentian, X. and Wang, Z. (2019) 'Study on ultrasonic techniques for enhancing the separation process of membrane', *Ultrasonics Sonochemistry*, 55, pp. 341–347. Available at: <https://doi.org/10.1016/j.ultsonch.2018.12.041>.

Zubov, A., Pokorný, J. and Kosek, J. (2012) 'Styrene–butadiene rubber (SBR) production by emulsion polymerization: Dynamic modeling and intensification of the process', *Chemical Engineering Journal*, 207–208, pp. 414–420. Available at: <https://doi.org/10.1016/j.cej.2012.06.144>.

Zulu, E., Ramasamy, S., Khoabane Sikhwivhilu, K. and Syampungani, S. (2025) 'A comprehensive review of recent advances in membrane innovations for efficient heavy metal removal

from mine effluents', *Scientific African*, 27, p. e02510. Available at: <https://doi.org/10.1016/j.sciaf.2024.e02510>.

Zuo, K., Wang, K., DuChanois, R.M., Fang, Q., Deemer, E.M., Huang, Xiaochuan, Xin, R., Said, I.A., He, Z., Feng, Y., Shane Walker, W., Lou, J., Elimelech, M., Huang, Xia and Li, Q. (2021) 'Selective membranes in water and wastewater treatment: Role of advanced materials', *Materials Today*, 50, pp. 516–532. Available at: <https://doi.org/10.1016/j.mattod.2021.06.013>.

Appendices

Appendix A

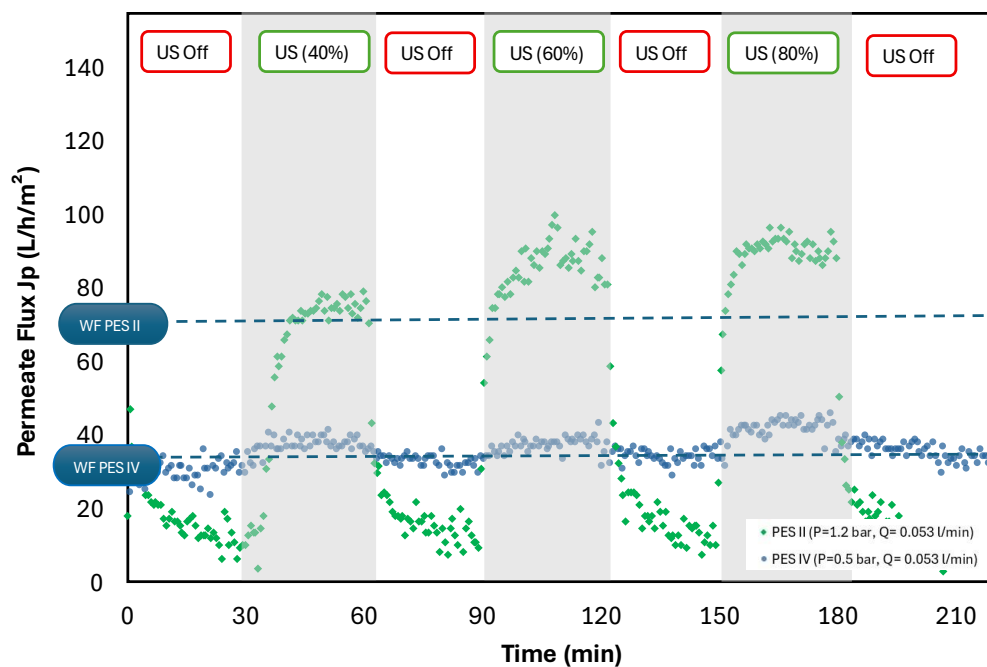


Figure A.1 Permeate flux of PES membranes II and IV during CNC filtration under US.

Appendix B

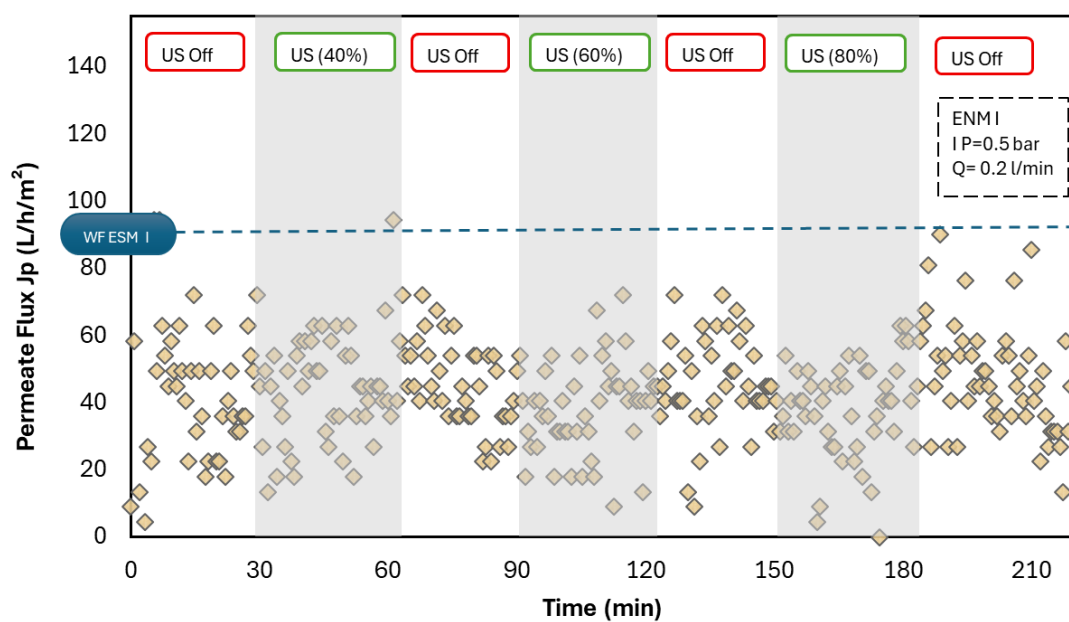


Figure B.1 The permeate flux of ENM I during CNC filtration under US.

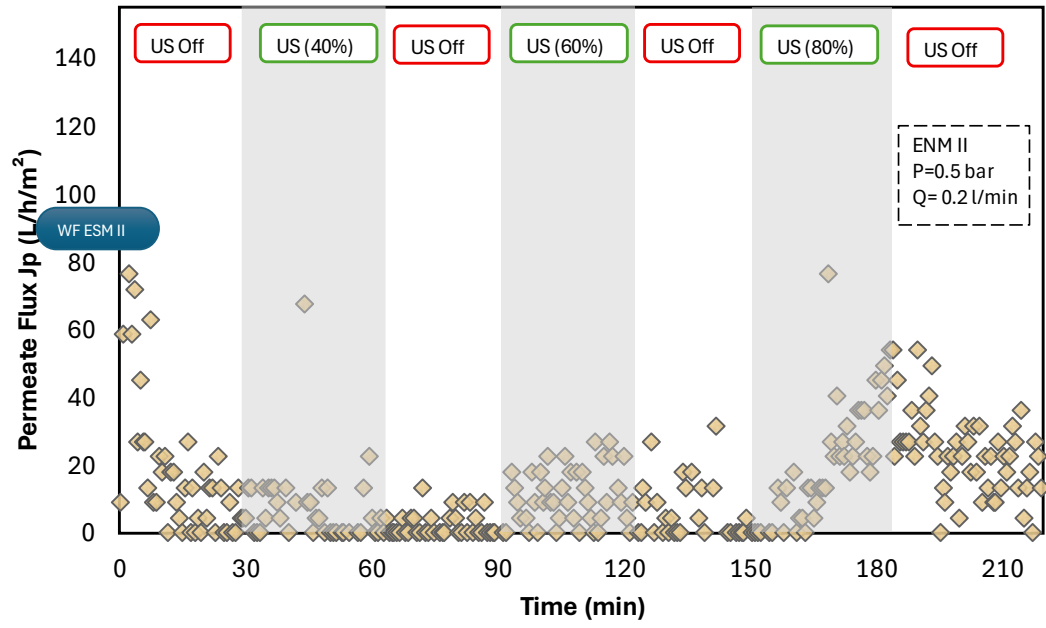


Figure B.2 The permeate flux of ENM II during CNC filtration under US.